Synthesis, Characterization, and Investigation of Non-covalent Interactions Between Novel Pyrene-appended Porphyrins and C60

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Anthony M. Wertish

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Dedication

I would like to dedicate this work to my entire family who have been my support and inspiration in the work that I do.

Abstract

Two different sets of novel pyrene-containing porphyrins were synthesized. The first set, which consists of asymmetric A_3B_1 and A_2B_2 porphyrins, was synthesized by the condensation of *t*-butylphenyl dipyrromethane and newly reported 4-(1-pyrenylmethoxy)benzaldehyde. The second set consists of asymmetric A_3B_1 and A_2B_2 porphyrins, which were synthesized by condensation of the dipyrromethane of the newly reported 4-(1-pyrenylmethoxy)benzaldehyde and 1-ferrocenecarboxaldehyde. All four porphyrins were fully characterized by UV-Vis-NIR spectroscopy, NMR spectroscopy, MCD spectroscopy and high-resolution mass spectrometry. Fluorescence spectroscopy studies were performed to qualitatively observe the interactions of the porphyrins with C_{60} fullerene. It was observed that C_{60} significantly quenches the fluorescence of pyrene, thus blocking fluorescence, suggesting there is a large amount of interaction between pyrene and C_{60}. DFT and TDDFT calculations were performed in order to further investigate the electronic structure and nature of the excited states of the target porphyrins by first optimizing the equilibrium geometries at the DFT level using the CAM-B3LYP exchange-correlation functional and furthermore using TDDFT. Transient absorption spectroscopy data is being analyzed to elucidate the electron transfer properties of the new porphyrins.

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List of Abbreviations

CNT	- Carbon Nanotube
DCM	- Dichloromethane
DDQ	- 2,3-dichloro-4,5-dicyanobenzoquinone
DFT	- Density functional theory
DSSC	- Dye Sensitized Solar Cell
DMF	- Dimethylformamide
EtOAc	- Ethyl Acetate
EtOH	- Ethanol
Fc	- Ferrocene
FTO	- Fluorine doped Tin Oxide
ITO	- Indium Tin Oxide
LED	- Light Emitting Diode
MeOH	- Methanol
Ph	- Phenyl
Por	- Porphyrin
Pyr	- Pyrene
TDDFT	- Time-dependent density functional theory
TEA	- Triethylamine
THF	- Tetrahydrofuran

Chapter 1 – Introduction

1.1. Overview of Organic Solar Cells

The world population has increased by nearly 200% since 1950 in which the standard of living increased overall as well.[1] The increase in population has driven the demand for energy at an almost identical rate, shown in Figure 1.[2] The high demand for energy has increased the burning of fossil fuels that emit CO_2 which damage the Earth's Ozone Layer.[3,4] As a result, the world has seen in increase in the demand for carbon-neutral energy generation technologies.[5]

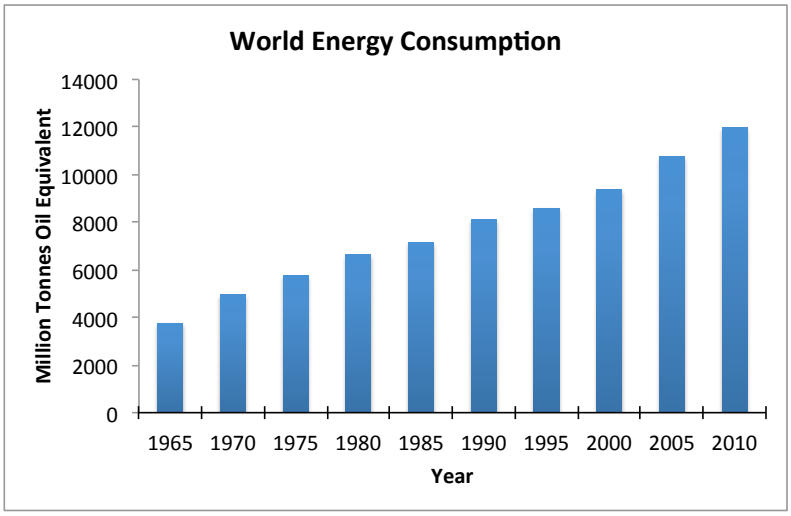

Figure 1. World energy consumption from 1965-2011.[2]

The field of organic-based and *green* chemistry has been growing immensely in the last decade[6], especially in the electronics industry. Organic-based commercial devices are gradually being introduced to consumers, proving it can be both economical and more environmentally friendly produce and use these devices.[7] As an alternative to using rare, costly, and hazardous metals, organic light emitting diodes (OLEDs) use carbon-based dyes that can be made both cheaply and abundantly.[7–9] OLEDs in general work by

applying an external voltage which causes charge recombination to occur at an interface between the two electrodes and light is emitted.[10] The reverse scheme can be applied to create a diode, which absorbs light and provides electric current, a solar cell.

Traditionally, silicon-based solar cells are used for industrial power generation. A typical silicon P-N junction contains electron-hole pairs when exposed to light.[11–13] It is the fundamental chemistry of these electron-hole pairs that causes current to flow to an applied load. Although P and N-doped silicon have proven to be reliable and a moderately efficient material for photocurrent generation, the ability to increase efficiencies becomes very expensive due to the manufacturing process.[14] In order to maintain the industry standard efficiency and decrease manufacturing cost, research has been pursued in the development of organic solar cells.[14,15] A schematic of a general design for an organic solar device is shown in Figure 2.

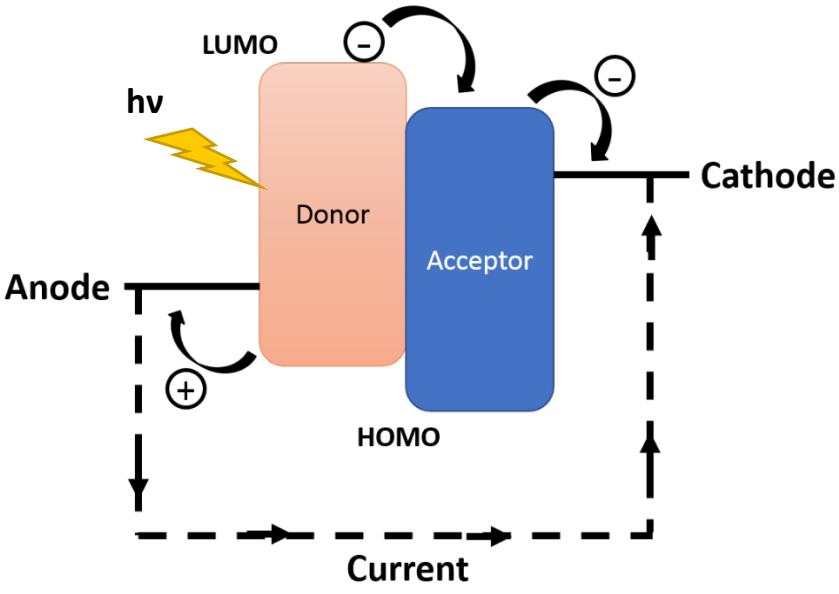

Figure 2. Schematic of a simple organic solar cell device.

The general design of an organic solar cell is similar to the P-N junction silicon solar device design, but instead of using P-N doped silicon, organic donor and acceptor molecules are employed.[12,13] The ability of the donor and acceptor to create a long-lived photo-induced charge separated state is one key factor that dictates the performance of the cell.[11] Another important factor is the charge mobility; there must be an effective medium to transport charge to the respective electrodes.[12] Most other factors impacting the devices performance can be fine-tuned through the fabrication process.[11,13,16,17]

Organic solar cells became a hot topic of research after Grätzel and colleagues created a dye-sensitized organic solar cell (DSSC) with 11.4% efficiency in the early 1990s.[16,18] The dye used in the first DSSCs was a ruthenium bipyridine based dye.[16] However, porphyrins have shown their potential as a photoexcited donor due to their very high molar absorbance near the maximum Sun irradiance.[19–21] By extending the π-conjugated system through the *meso* position on the porphyrins, researchers have broadened the spectral absorbance of porphyrins and exceeded 13% efficiency with using the DSSC template shown in Figure 3.[19] In addition, the optimization of device fabrication has been thoroughly researched, thus allowing easy comparison between novel chromophoric donors.[11,13,16,17] Although the DSSC design shows promising efficiency, it lacks economic durability due to the use of liquid electrolytes that must be completely sealed within the device.[11] Thus the device is rigid and the electrolyte is prone to evaporation if not sealed properly. Some gel and polymer electrolytes have been studied but have found to have lower efficiencies due to the lack of mobility of the charge carriers.[12,22]

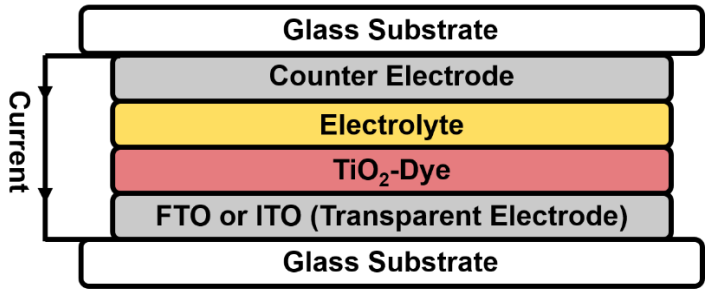

Figure 3. General design of a DSSC.[12]

An alternative to the DSSC approach is the development of solid-state organic solar cells.[23,24] The construction of these devices can vary immensely. In the simplest form, the bilayer device consists of conducting polymers and an active (light absorbing) layer met at a uniform interface at which the photocurrent is generated. These bilayer devices can be fabricated very easily and affordably, however layers must be very thin (5-20 nm) to facilitate electron-hole pair transport.[25] This limits the device's photoactive surface area and restricts the overall performance.[25]

Adding to the bilayer design are bulk heterojunction (BHJ) solar cells. These devices are similar to that of the bilayer device but instead of having a uniform planar surface contact, the polymer and active layer are blended into a bulk composite.[23,24] This allows a substantial increase in the surface area of the active layer which allows a higher solar flux and enhances the device's performance.[24] Devices typically employ a polymer electron donor with C_{60} fullerene acceptors.[26] The largest drawback to BHJ solar devices is that charge recombination is much more likely due to the non-uniform mixture and low separation distances.[24] Attempts have been and are being made to make these devices much more efficient but have yet to achieve the efficiencies of DSSCs.[23]

So far I have discussed the basic structure of organic solar devices that have been developed over the past 25 years. Recently, a novel approach using carbon-based

acceptors to construct solar devices has been employed.[27–32] Graphene, carbon nanotubes (CNTs), and fullerenes have been shown to exhibit favorable properties for electron-hole pair generation as well as charge transport.[31,33,34] Not only do these nano-scale materials display exceptional characteristics but they also can be made cheaply from abundant precursor materials.[32]

In 2004, researchers found that employing CNTs on the TiO_2 surface for DSCs improved the device's ability to mobilize electrons and increase short-circuit current density by 25%.[28] One drawback when using this CNT/TiO_2 mixture is that the dye being used will not have as many active sites to bind to the TiO_2 since CNTs occupy that space. Due to its high conductivity, graphene has also been used to facilitated charge mobilization and showed even better performance than CNTs.[32] Many BHJ solar cells use soluble C_{60} fullerene derivatives as electron acceptors as well.[26,27]

In addition to their exceptional properties, these large conjugated π-systems have very strong intermolecular attractions to other extended π-systems. The Van der Waals forces are so great between large π-systems that researchers have labelled them as π-π bonding or π-stacking.[35–37] Molecules with high planarity and aromaticity show the best ability to partake in π-stacking.[35] One such molecule is pyrene, an aromatic molecule consisting of four fused rings which is commonly used as a tag for fluorescence probing, which has high planarity and shows great ability to bind to other conjugated systems through π-stacking.[33,35,38–40] Theoretical studies have found the binding energy of pyrene to graphene to be near 26.5 kcal/mol.[35] Another study calculated the binding energy of 1-methylpyrene to be 17.5 kcal/mol when binding to zig-zag(10,0) single-walled carbon

nanotubes.[37] Although the results of these two experiments are vastly different, they provide insight into the impressive strength of these π-π interactions.

To date, most research involving electron transfer for applications in solar devices has been done on dyad and triad systems that employ C_{60} via covalent linkage.[41–44] Although this method provides a distinct photo-induced electron transfer to C_{60} to yield a $Dye^{+\bullet} \cdots C_{60}{}^{-\bullet}$ charge separate species[45–47], it adds a step to the device fabrication that may not be necessary. If it is possible to create the charge separated species via non-covalent linking, we will be able to circumvent the synthesis of the dyads by allowing self-assembly to occur in the fabrication process. This could potentially decrease production cost as well as increase the order of the device's composition.

1.2. Introduction to Porphyrin Synthesis

Porphyrin synthesis was largely pioneered by Paul Rothemund in the 1930s in which a sealed bomb capsule was used to create tetraphenyl porphyrin from benzaldehyde and pyrrole.[48] The method was so harsh that very few substituted aldehydes could withstand the reaction conditions and led to very low yields.[49] In the 1960s, Alan Adler and Frederick Longo designed a more efficient method to synthesize substituted porphyrins. Their method consisted of combining pyrrole with benzaldehyde in propionic acid and refluxing for 30 minutes.[50] Relatively high yields, near 20%, have been achieved using this methodology but the high temperature of reflux (141^{o}C) presents a setback for aldehydes with low thermal stability. In the 1980s, Lindsey and colleagues created a method complimentary to the Adler-Longo method. This new method consists of the condensation of an aldehyde and pyrrole, using a Lewis acid

catalyst.[49] Their method works under three major facets. First, the porphyrinogen is the thermodynamically favored product of condensation, which can be irreversibly oxidized after equilibrium is reached. Second, pyrrole and the aldehyde are reactive species, making high temperatures unnecessary. Third, the reaction conditions are suitable for a wide variety of aldehydes. Porphyrin yields have been reported near 40% using the Lindsey method.[49] A comparison of the three reactions schemes is shown in Figure 4**.**

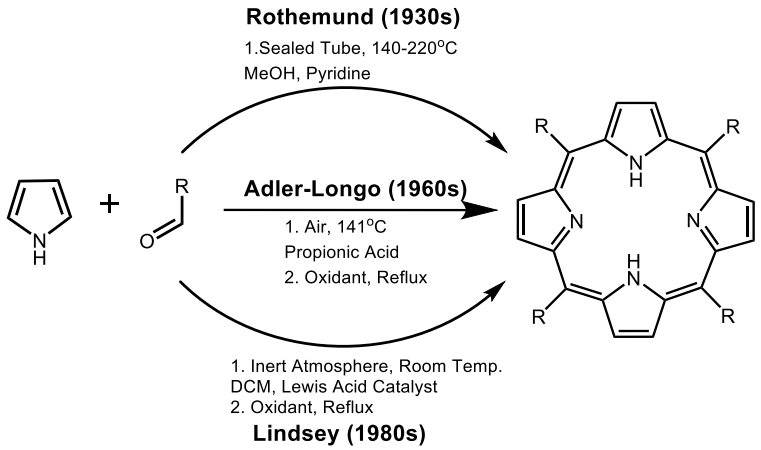

Figure 4. Porphyrin synthesis reaction schemes.

The Lindsey method typically employs a chlorinated solvent such as dichloromethane and a Lewis acid catalyst (such as trifluoroacetic acid, BF_3•Et_2O, or BCl_3).[49] Because the formation of the porphyrinogen intermediate is in equilibrium with competing oligomer and polymer reactions, strict control over the concentration of reactants is require to prevent such oligomerization and polymerization. Reactants of 10^{-2} M equimolar concentrations and 10^{-3} M catalyst provided the best yields.[49] The $6e^-/6H^+$ oxidation reaction is carried out using excess oxidants (such as *p*-chloranil or 2,3-dicchloro-4,5-dicyanobenzoquinone (DDQ)) at reflux conditions.[49]

When asymmetric porphyrins are desired, synthesis can become much more complex. In simplest form, using two aldehydes at $5x10^{-3}$ M and pyrrole at 10^{-2} M will provide a statistical distribution of six possible products, which can be very cumbersome to isolate.[51] A more efficient approach is to create a dipyrromethane from one aldehyde followed by reacting that dipyrromethane with the other aldehyde.[51] This method should provide only one porphyrin with alternating, ABAB, aldehydes on the *meso* position. However, due to the intermediate equilibrium reactions, it is possible to have scrambling, which causes a flip at the *meso* position and leads to AABB substitutions as well as other possible substitution patterns.[51,52] Purification of reaction mixtures typically consists of the neutralization of the acid using an organic base followed by column chromatography or sublimation.[49,51] If multiple porphyrins are created, column chromatography may become significantly more difficult if there is poor resolution. It may be necessary to use preparative TLC and very specific solvent systems in these situations.

1.3 Overview of Study

The aim of this research was to design, synthesize, and investigate a porphyrin capable of excellent light absorption as well as the ability to interact non-covalently with large π-systems such as fullerenes. The porphyrin core structure was used since it can be easily functionalized and has good thermal, chemical, and photochemical stability. The porphyrin should absorb intensely at or near the maximum solar irradiance (~480 nm), be soluble in common organic solvents, and have the ability to interact with other π-systems such as Fullerenes, CNTs, and graphene. In order to provide sufficient interaction with other π-systems, pyrene derivatives were attached at the *meso* positions of the porphyrin.

In addition, to help aid in electron transfer I aim to create porphyrins with ferrocenes at different *meso* positions. Figure 5 depicts the theoretical approach to the research presented here.

Two sets of porphyrins were synthesized. The first set consisted of P_1B_3 and P_2B_2 substituted pyrene (P) and *t*-butylphenyl (B) fragments attached at the *meso*-position. The second set consisted of P_1Fc_3 and P_2Fc_3 substituted pyrene (P) and ferrocene (Fc) fragments attached at the *meso*-position. The properties of each porphyrin were characterized by NMR, HRMS, UV-Vis-NIR, MCD, fluorescence, and FT-IR spectroscopy. The non-covalent interactions of the porphyrins with C_{60} fullerene were analyzed by UV-Vis and Fluorescence spectroscopy. Transient absorption spectroscopy experiments have been performed and are presented here as preliminary data. One specific question to investigate is whether or not non-covalent interactions in solution are significant enough for photo induced electron transfer to an acceptor molecule to occur.

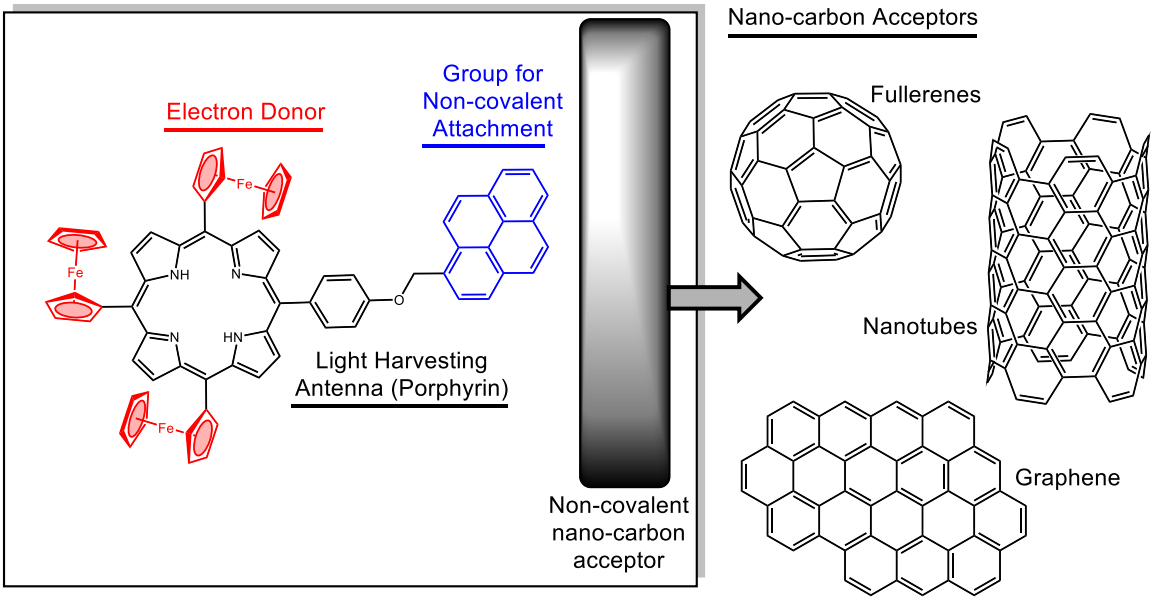

Figure 5. Diagram of proposed theoretical donor-acceptor approach.

Chapter 2 – Materials and Methods

2.1. Physical Measurements

All NMR spectra were recorded using a Varian INOVA instrument with 500 MHz frequency for protons and a 125 MHz frequency for carbons. Chemical shifts are reported in ppm and referenced to an internal TMS standard. Mass spectra were recorded on a Bruker MicroTOF III high-resolution mass spectrometer using electrospray ionization approach. UV-Vis-NIR data were recorded with a Jasco V-670 spectrometer with toluene as a solvent unless otherwise stated. MCD data were obtained using an OLIS DCM 17 CD spectropolarimeter equipped with a permanent 1.4T DeSa magnet. The spectra were recorded twice for each sample, once with a parallel field and again with an antiparallel field, and their intensities were expressed by molar elipticity per T = $[\Theta]_M$/deg dm^3 mol^{-1} cm^{-1} T^{-1}. Fluorescence data was acquired using a Varian, Cary Eclipse fluorescence spectrophotometer at 25^oC. Infrared spectroscopy data were acquired using a PerkinElmer Spectrum 100 FT-IR spectrometer.

2.2. Computational Details

All Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations were conducted using the Gaussian 09 software.[53] The starting geometries of the porphyrin molecules were optimized at the DFT level using CAM-B3LYP exchange-correlation functional.[54] Equilibrium geometries were confirmed by frequency calculations and specifically by the absence of imaginary frequencies. Atoms were modelled using the 6-31g(d) basis set.[55] For the DFT and TDDFT calculations, solvent effects were calculated using the PCM approach with DCM as a solvent.[56] In the TDDFT

calculations, the first 80 states were calculated for porphyrins **1a** and **2a** while 120 states were calculated for porphyrins **1b** and **2b** (Figure 6). Molecular orbital contributions were compiled from single-point calculations using the QMForge software.[57]

2.3. Materials

All reactions were performed under argon atmosphere unless otherwise stated. Dichloromethane was dried and distilled over calcium hydride. THF was dried over sodium with benzophenone indicator then freshly distilled prior to use. Toluene was dried over sodium and distilled before using. Dimethylformamide was dried over 4Å molecular sieves for at least 2 full days. Pyrrole was purchased from Millipore Corporation and distilled under vacuum before use. 1-pyrenecarboxaldehyde, phosphorus tribromide, 4-hydroxybenzaldehyde, and 4-*t*-butylbenzaldehyde were purchased from Alfa Aesar and used as received. Sodium borohydride and ferrocene carboxaldehyde were purchased from Acros Organics and used as received. Silica TLC plates (20x20cm, Aluminum back, fluorescent indicator, 25μm particles) and Aluminum oxide (activated, basic, Brockmann I, Standard grade, 150 mesh, 58Å) were purchased from Sigma Aldrich.

2.4. Synthesis

The following paragraphs describe the specific procedures and methods used in each step of the synthetic scheme, which is summarized in Figure 6. Numbers in parenthesis corresponds the respective molecule shown in Figure 6.

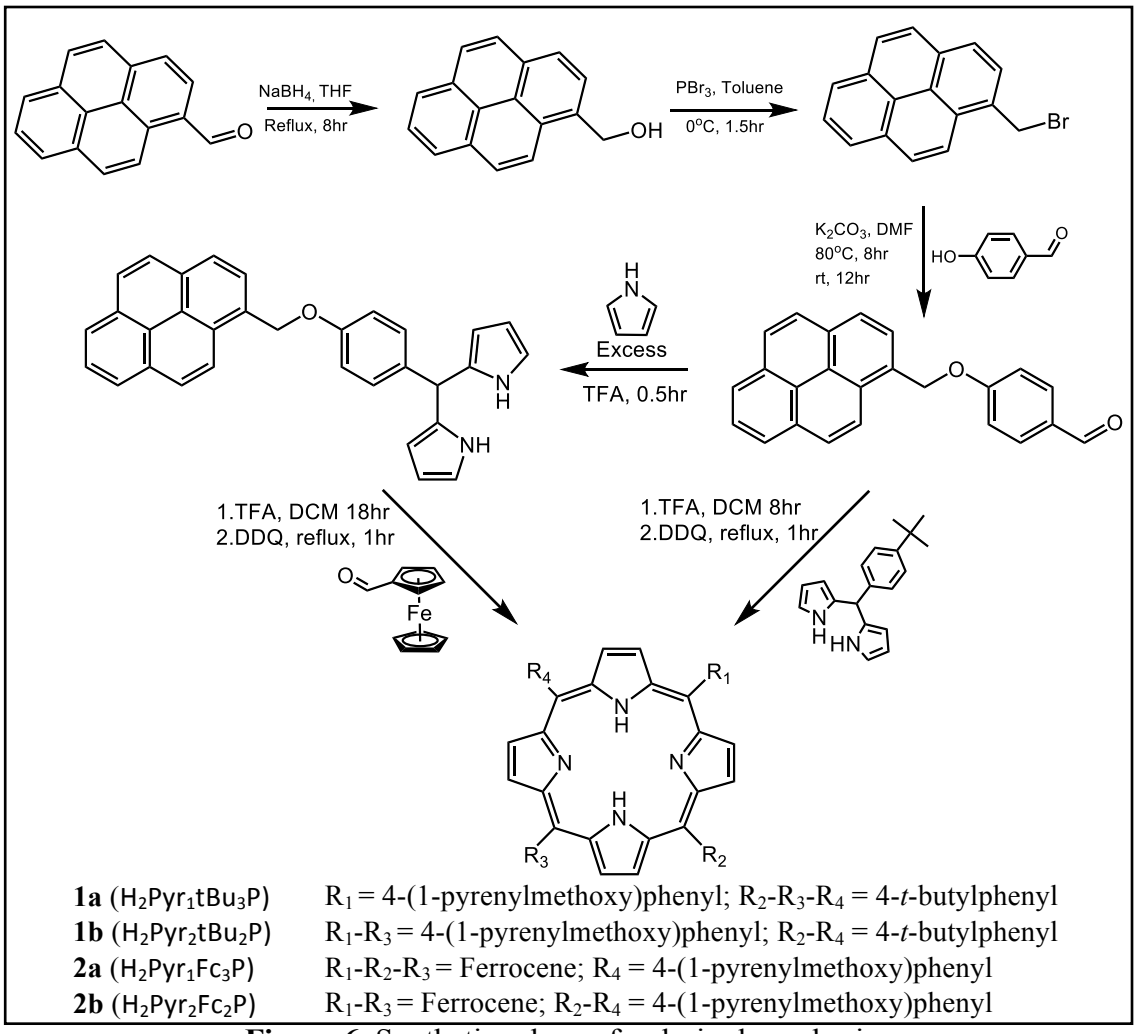

Figure 6. Synthetic scheme for desired porphyrins

*1-pyrenemethanol (**3**)*[58,59]

A 250 mL Schlenk flask was charged with 1-pyrenecarboxaldehyde (8.053 g, 34.97 mmol) in 100 mL of dry THF. Sodium borohydride (3.062 g, 80.94 mmol) was then added to the reaction mixture in one portion. The reaction flask was fitted with a water condenser and refluxed for 8 hours. The reaction solution was then cooled to room temperature and left to react overnight (14 hours). 15 mL of 1.0M hydrochloric acid was slowly added to the reaction mixture. The product was extracted using dichloromethane, washed with 5% Na_2CO_3 solution (2 X 20 mL), dried over Na_2SO_4, and evaporated to

afford 7.127 g (30.55 mmol) of off-white product. Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 9.2 Hz, 1H), 8.22 – 8.18 (m, 2H), 8.15 (dd, *J* = 8.5, 2.3 Hz, 2H), 8.08 – 7.99 (m, 4H), 5.40 (d, *J* = 4.3 Hz, 2H), 1.90 (t, *J* = 4.9 Hz, 1H)]

*1-(bromomethyl)pyrene (**4**)*[59]

To a 100 mL Schlenk flask, 1-pyrenemethanol (2.061 g, 8.83 mmol) was added, followed by 40 mL of dry toluene. The reaction flask was heated to approximately 80°C to aid in the dissolution of 1-pyrenemethanol. The reaction solution was then placed into an ice water bath and cooled to 0°C. Phosphorus tribromide (450 μL, 4.74 mmol) was added slowly via syringe to the reaction mixture. The reaction was stirred under argon for 1.25 hours. The yellow/brown mixture was warmed to room temperature and saturated Na_2CO_3 (15 mL) was added slowly. The organic layer was further washed with distilled water (2 X 25 mL) and once with brine (10 mL), then dried over anhydrous sodium sulfate. A yellow/brown solid was obtained after evaporation (1.473 g, 4.99 mmol). Yield: 57%. [^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.2 Hz, 1H), 8.29 – 8.20 (m, 3H), 8.15 – 8.01 (m, 5H), 5.27 (s, 2H)]

*4-(1-pyrenemethoxy)benzaldehyde (**5**)*[60,61]

In a 50 mL Schlenk flask, potassium carbonate (4.021 g, 29.09 mmol) and 4-hydroxybenzaldehyde (0.901 g, 7.38 mmol) were dissolved in 25 mL of dimethylformamide. To the reaction mixture, 1-(bromomethyl)pyrene (1.633 g, 5.53 mmol) was then added in one portion. The solution was heated to 80°C for 4 hours and then reacted at room temperature for 16 hours. The reaction solution was poured into 125 mL of distilled water. The orange/yellow precipitate was filtered and washed twice with

distilled water (2 X 25 mL). The precipitate was then dissolved in dichloromethane, dried over Na_2SO_4, and evaporated. The dry product was then recrystallized from chloroform and hexanes to afford a beige product (1.345 g, 4.00 mmol). Yield: 72%. MP = 153-156^{o}C. [^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 8.26 – 8.17 (m, 4H), 8.13 – 8.04 (m, 4H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 5.86 (s, 2H).] Anal. Calc'd for Molecule **5** ($C_{24}H_{16}O_2$ X 0.08 C_6H_{14} X 0.06 $CHCl_3$): C, 84.07; H, 4.94. Found: C, 84.06; H, 4.94; $CHCl_3$, 0.06%; C_6H_{12}, 0.09%.

*Dipyrromethane **6*** [62]

To a 50ml Schlenk flask, 210 mg (0.595 mmol) of molecule **5** and 7 ml (72 mmol) of freshly distilled pyrrole were added and stirred under argon. After 5 minutes 15 μL of trifluoroacetic acid (TFA) was added via syringe to the reaction mixture. The light yellow solution turned slightly darker yellow upon addition of TFA. The reaction was let stir at room temperature under argon for 45 minutes. 5 mL of 1M NaOH was then added and the organics were extracted with dichloromethane (2 x 10 mL), dried over sodium sulfate, and evaporated. The product was then dissolved in 2 mL of DCM then crashed into 80 mL of hexanes and filtered through a membrane filter to afford 160 mg (0.354 mmol) of dipyrromethane **6**. Yield: 60% [^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.2 Hz, 1H), 8.21 (dd, *J* = 7.6, 3.1 Hz, 2H), 8.16 (dd, *J* = 13.1, 8.5 Hz, 2H), 8.11 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 3.3 Hz, 2H), 8.03 (t, *J* = 7.6 Hz, 1H), 7.92 (s, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 4.1, 2.5 Hz, 2H), 6.18 (dd, *J* = 5.8, 2.8 Hz, 2H), 5.95 (s, 2H), 5.73 (s, 2H), 5.45 (s, 1H).]

Dipyrromethane 7 [62]

To a 50 mL round bottom flask, pyrrole (10 mL, 144 mmol), *t*-butylbenzaldehyde (850 μL, 5.1 mmol) were added and stirred with a magnetic stirrer. Trifluoracetic acid (100 μL, 1.3 mmol) was added to the reaction mixture. The solution turned red upon the addition of TFA. The reaction was allowed to react at room temperature for 25 minutes. The reaction was then quenched with 1M NaOH (10 mL) and turned yellow. Organics were extracted using dichloromethane, then dried over Na_2SO_4. The product was isolated using a short silica column and dichloromethane as the eluent. The quick-eluding clear product was dried to achieve 0.780 g of off-white product. The product was used immediately upon complete synthesis. Yield: 55%.

*Porphyrins **1a** & **1b***[49,51]

A 250 mL Schlenk flask was charged with 4-(1-pyrenemethoxy)benzaldehyde (0.496 g, 1.47 mmol) and dipyrromethane **7** (0.491 g, 1.76 mmol) in dry dichloromethane. Trifluoroacetic acid (20 μL, 0.26 mmol) was added via syringe to the reaction mixture. The solution turned slightly darker yellow upon addition. The solution was let react at room temperature for 1.75 hours. DDQ (0.486 g, 2.14 mmol) was then added to the dark red reaction solution and let react for 45 minutes at reflux. The reaction mixture was cooled to room temperature and 1.0 mL of triethylamine (TEA) was added to neutralize the acid and deprotonate the porphyrin. The product was concentrated and ran through a short alumina column using DCM:triethylamine (100/1, v/v) as the eluent. The porphyrin fractions eluded as red fractions with pink fluorescence in solution. The collected fractions of porphyrin were combined. A long alumina column (10 cm long by 2 cm diameter) was used to separate the porphyrin fractions, using toluene:triethylamine

(100/1, v/v) as the eluent. Fraction 1 was a green solution that dried to purple. Fraction 2 was a dark red solution that dried to a purple/brown mixture. Fraction 3 was eluded by increasing polarity with ethyl acetate (toluene/EtOAc/TEA, 100/5/1, v/v). The 3rd fraction was collected as a dark brown-red solution. Each fraction was further purified by recrystallization in hexanes to afford a purple precipitated. UV-Vis was employed to verify the presence of pyrene on the porphyrin. Fraction 2 afforded 51 mg of porphyrin **1a** (7% yield). Fraction 3 afforded 35 mg of porphyrin **1b** (4% yield). ^{1}H NMR and HRMS spectra are discussed in Chapter 3.

*Porphyrins **2a** & **2b***[49,51]

230mg (0.510mmol) of dipyrromethane **6**, 108 mg (0.500 mmol) of ferrocene carboxaldehyde, and 50 mL of freshly distilled DCM we combined into a 100 ml Schlenk flask and stirred under argon for 5 minutes. 15 μL of trifluoroacetic acid was then added to the reaction mixture via syringe. The solution turned darker red upon TFA addition. The reaction was let stir at room temperature for 24 hours. To the dark red solution, 123 mg (0.540 mmol) of DDQ was added and the solution was refluxed for 1.75 hours then cooled to room temperature and 1 ml of triethylamine was added. The crude mixture was concentrated and then partially purified using column chromatography on Alumina with DCM:TEA (100/, v/v) as the eluent. The quickly eluding green fraction containing the desired porphyrins was concentrated and further purified using multiple 20x20cm silica TLC plates with DCM/toluene/EtOAc (12:8:1) as the eluent. The leading green fraction contained a mixture of substituted porphyrins and was not further purified. The second and third green fractions contained *trans*-**2b** and *cis*-**2b**, respectively. The fourth green

fraction contained **2a**. All products were removed from silica by filtering through a fritted funnel with dichloromethane:EtOAc (9:1). ^{1}H NMR and HRMS spectra are discussed in Chapter 3.

Chapter 3. Results and Discussion

3.1. Synthesis

The complete synthesis of the porphyrins is a five step, bottom-up approach. The first three steps of the synthesis are devoted to the synthesis of the desired aldehyde, which contains the pyrene fragment. First, commercially available 1-pyrenecarboxaldehyde was reduced using sodium borohydride to form 1-pyrenemethanol (**3**) in moderate to high yields. Following reduction, the alcohol (**3**) was then converted to the bromo-derivative (**4**) using phosphorus tribromide in order to increase the ability to undergo nucleophilic substitution with 4-hyrdoxybenzaldehyde under basic conditions to form aldehyde **5**. Moderate yields were observed at both the bromine halogenation and substitution reactions. In order to create the desired porphyrins, dipyrromethanes **6** and **7** were synthesized by using a large excess of pyrrole in order to control the reaction equilibrium, thus allowing the target dipyrromethane as the major product. By creating half of the porphyrin prior to full synthesis, I was able to selectively choose where each substituent would be placed. However, the reaction mechanism for synthesis of a porphyrin is moderately complex and contains many steps in equilibrium, therefore scrambling can occur.[51,52] Through the use of mass spectrometry and ^{1}H NMR it was observed that porphyrins such as 5,10,15,20-tetra[4-(1-pyrenylmethoxy)phenyl] porphyrin, 5,10,15,20-tetraferrocenyl porphyrin, 5,10,15-tri[4-(1-pyrenylmethoxy)phenyl]-20-(4-*t*-butylphenyl) porphyrin, 5,10-diferrocenyl-15,20-di[4-(1-pyrenylmethoxy)phenyl] porphyrin, and 5-ferrocenyl-10,15,20-tri[4-(1-pyrenylmethoxy)phenyl] porphyrin, were also synthesized. However, due to low yields

and difficulty in purification, these porphyrins were not pursued any further. Evidence for these claims can be found in the Supporting Information, Figures S2-S4.

One major issue which arose during the synthesis is which acid catalyst to use for the porphyrin reaction. Boron trifluoride diethyl etherate, propionic acid, and trifluoroacetic acid were all used in attempts to create the porphyrins however trifluoroacetic acid was the only catalyst to provide significant yields. Also, issues arose when attempting to use ferrocene dipyrromethane with aldehyde **5** to synthesize the porphyrin **(**Figure 7). The majority of porphyrin created was tetraferrocenyl porphyrin, with very little or none other porphyrins created. Since the reaction mechanism consists of many reversible steps, the intermediates may rearrange and eliminate the pyrene aldehyde and show preference to the more reactive ferrocene intermediates. In order to circumvent the problem, dipyrromethane **6** was synthesized and used with commercially available ferrocene carboxaldehyde to create the desired porphyrins, as shown in the scheme in Figure 6. Scrambling still occurs but to a much lesser degree than when using the initial synthetic route.

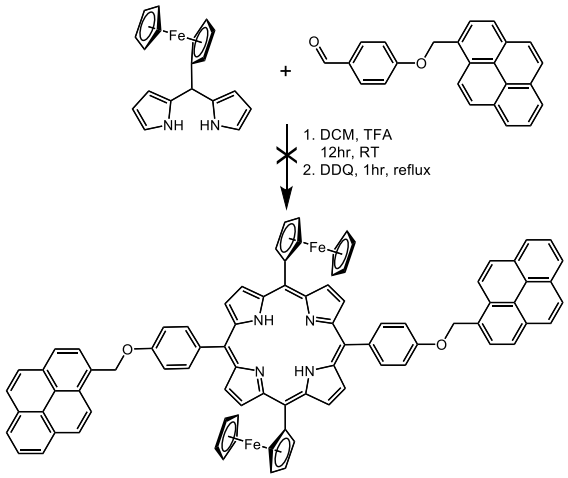

Figure 7. Initial reaction scheme pursued. Yielded mostly tetra-ferrocenyl porphyrin and very little desired porphyrins.

The most significant drawback to this synthesis is the separation of the ferrocenyl porphyrins. Extremely careful chromatography techniques were used in order to get well-resolved separation and pure porphyrin molecules. It was critical, during separation on TLC plates that the eluent be replaced in a timely manner due to polarity changes caused by evaporation. In addition, all of the target porphyrin molecules are all soluble in toluene and dichloromethane, however heat and/or sonication may be necessary to solvate any crystallized molecules.

3.2. NMR, FT-IR, and HRMS Spectra

In all the ^{1}H and ^{13}C NMR spectra, signal integrations match the molecular structure and peak assignments very well. All asterisks on the spectra represent solvent impurities. Pyrene typically shows a mix of signals on the ^{1}H NMR between 8.0 and 8.5 ppm from its nine protons. Furthermore, a sharp singlet is observed between 5.2 and 6.1 ppm from the aliphatic $-CH_2-$ group at the 1-pyrenyl position.

Molecule **3** (Figure 8). After reduction of 1-pyrenecarboxaldehyde with sodium borohydride, the OH signal at 1.90 ppm with low resolved triplet appears on the ^{1}H NMR spectra. In addition, the $-CH_2-$ singlet is split into a doublet with a low coupling constant (J = 4.3 Hz) because of the hydroxyl proton.

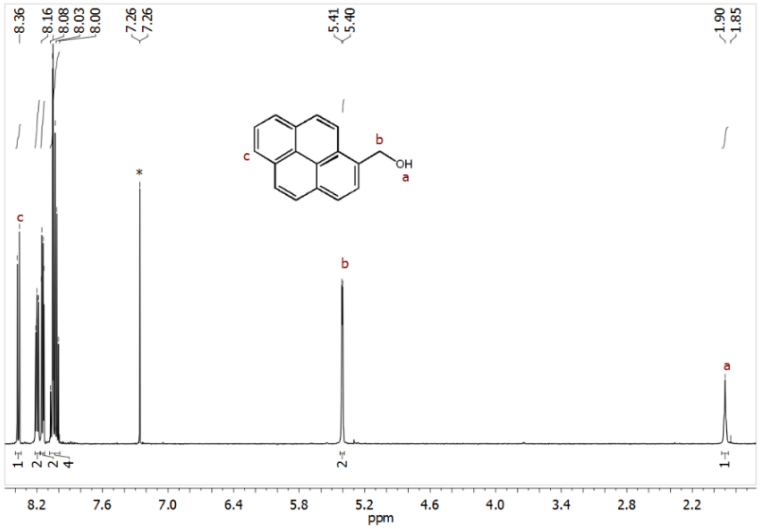

Figure 8. ^{1}H NMR of 1-pyrenemethanol (**3**) in $CDCl_3$.

Molecule **4** (Figure 9). After halogenation of the alcohol with phosphorus tribromide to the bromo derivative (**4**), the -CH_2- signature is shifted upfield from 5.40 ppm to 5.27 ppm, which indicates a lesser deshielding effect from the bromine atom compared to the hydroxyl group. In addition the doublet at 5.40 ppm becomes a singlet, which provides evidence of the substitution of the hydroxyl group with bromine.

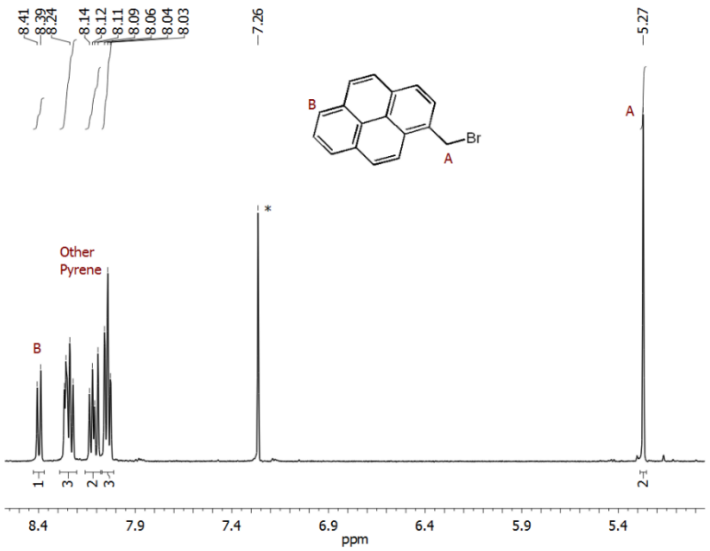

Figure 9. ^{1}H NMR of 1-(bromomethyl)pyrene (**4**) in $CDCl_3$.

Molecule **5** (Figures 10-12). The proton NMR of the newly reported aldehyde (Figure 10) shows the appearance of both the aldehyde singlet (9.92 ppm) and two phenyl proton doublets (7.23 ppm and 7.89 ppm). The aliphatic protons are shifted downfield from 5.27 ppm to 5.86 ppm. The ^{13}C NMR of 4-(1-pyrenylmethoxy)benzaldehyde (Figure 11) contains twenty-two distinct carbon signatures. This corresponds to all twenty-four carbons of the target molecule, with four of the phenyl carbons sharing two signals due to symmetry. In addition, both the aldehyde (191 ppm) and aliphatic carbon (69 ppm) signatures show definitive evidence of the target molecule. An intensity at 1682 cm^{-1} on the IR spectrum (Figure 12) represents the characteristic signature of an aldehyde.

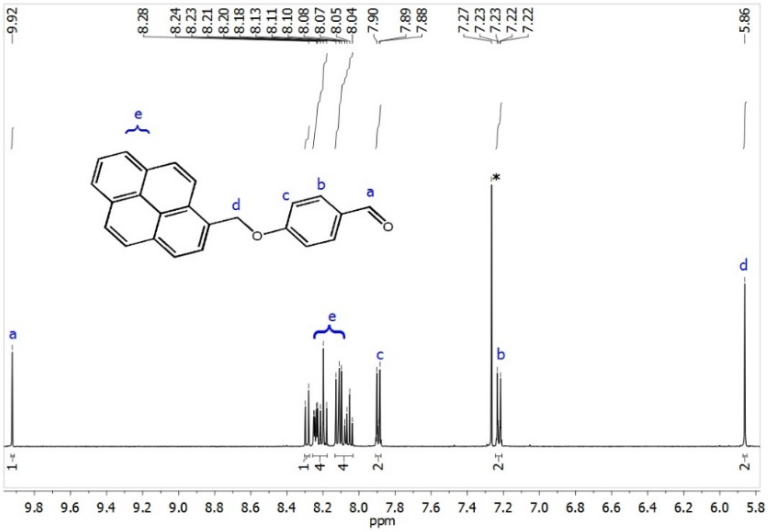

Figure 10. ^{1}H NMR of 4-(1-pyrenylmethoxy)benzaldehyde (**5**) in $CDCl_3$.

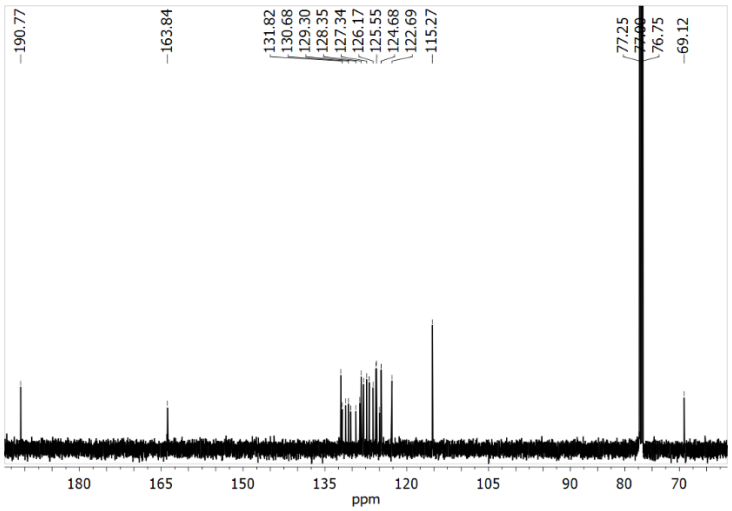

Figure 11. ^{13}C NMR of 4-(1-pyrenylmethoxy)benzaldehyde (**5**) in $CDCl_3$.

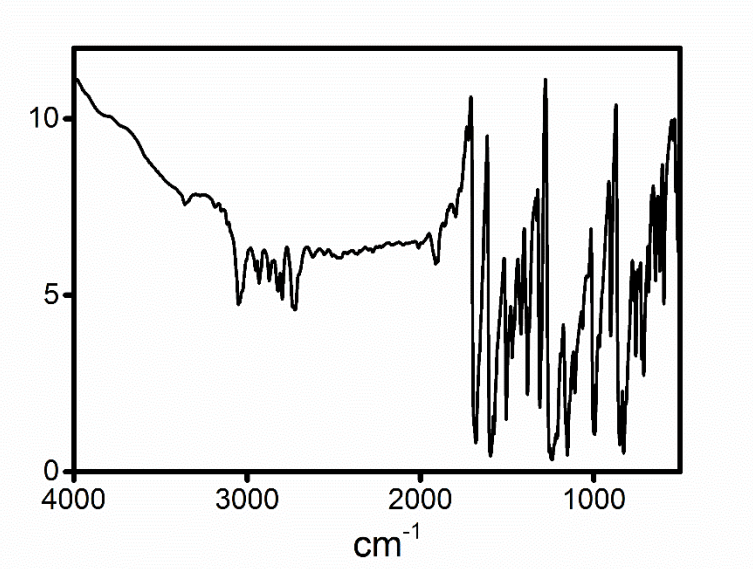

Figure 12. FT-IR of aldehyde **5** in a KBr pellet. Carbonyl present at 1682 cm^{-1}.

Molecule **6** (Figure 12). The newly reported dipyrromethane shows a multitude of chemical shifts and aromatic signals, which have been assigned in Figure 12 to their respective proton(s). The NH signal is easily seen at 7.92 ppm as a broad singlet. The shift in the aliphatic hydrogen signal from 5.86 to 5.45 ppm indicates the formation of the product and the lack of unreacted reactants.

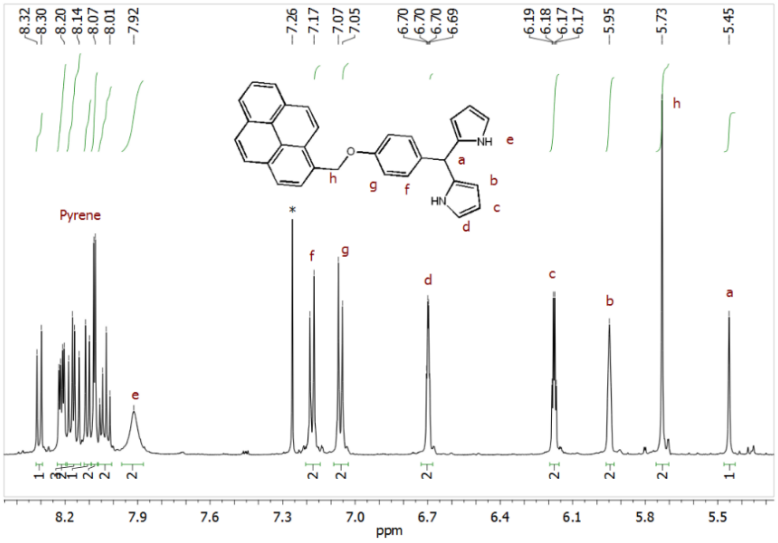

Figure 13. ^{1}H NMR of molecule **6** in $CDCl_3$.

Porphyrin **1a** (Figures 14-16). The ^{1}H NMR (Figure 14) and the complimentary COSY NMR (Figure 15) indicate the successful synthesis and purification of the target porphyrin **1a**. The NH signals appear highly shielded and upfield (-2.72 ppm) which is typical for porphyrins due to the diatropic ring current.[45,63] The COSY NMR unveils the coupling of neighboring protons and allows the assignment of signals b, c, and g (Figure 15) to be distinguished from each other. The integration of the chemical shifts indicated a 3:1 *t*-butylphenyl to pyrene substituted porphyrin, confirming the target porphyrin, **1a**. The HRMS of porphyrin **1a** (Figure 16) shows excellent agreement with the predicted spectra and isotope abundances.

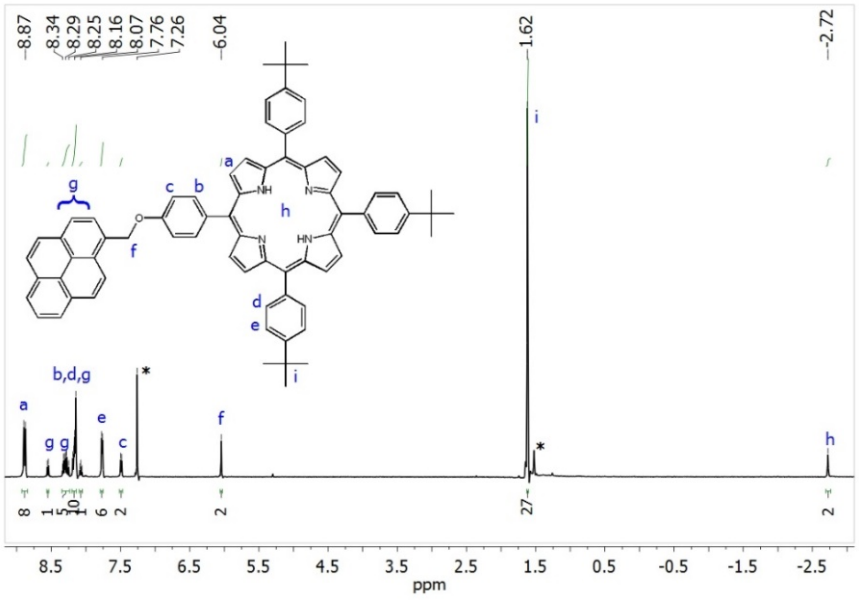

Figure 14. ^{1}H NMR of Porphyrin **1a** in $CDCl_3$.

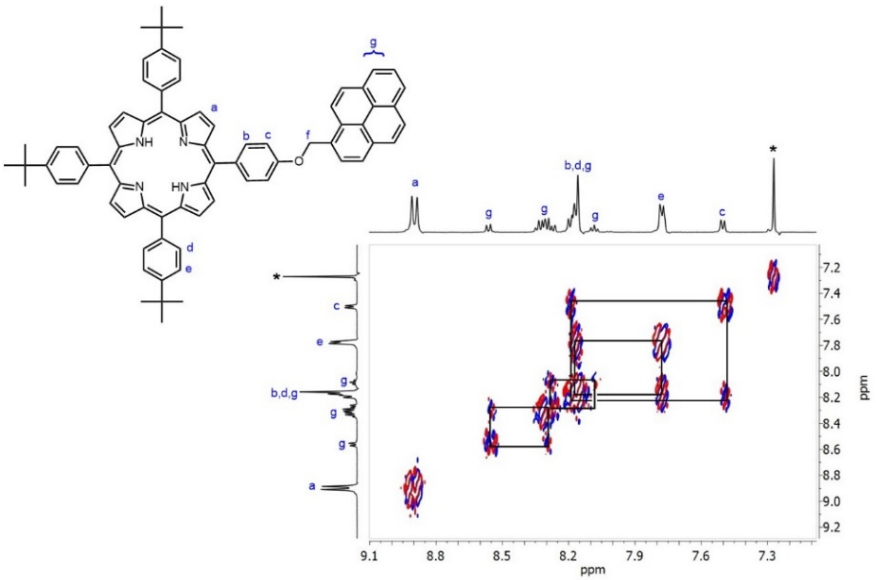

Figure 15. COSY NMR of porphyrin **1a** in $CDCl_3$.

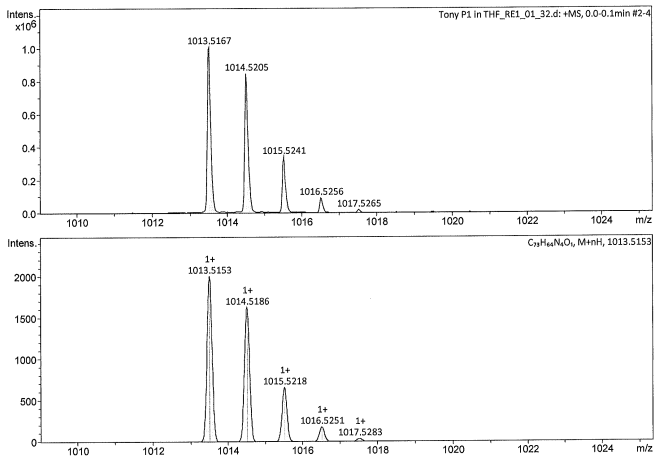

Figure 16. High-resolution mass spectrum (HRMS) of porphyrin **1a**. Experimental spectrum at top, predicted spectrum at bottom.

Porphyrin **1b** (Figures 17-19). The ^{1}H NMR (Figure 17) and complimentary COSY NMR (Figure 18) indicate the successful synthesis and purification of the target porphyrin **1b**. The NH signals appear highly shielded and upfield (-2.71 ppm). The COSY NMR unveils the coupling of neighboring protons and allows the assignment of signals b, c, and g (Figure 18) to be distinguished from each other. Integration of the chemical shifts indicated a 2:2 *t*-butylphenyl to pyrene substituted porphyrin. The HRMS of porphyrin **1b** (Figure 19) shows excellent agreement with the predicted spectra and isotope abundances.

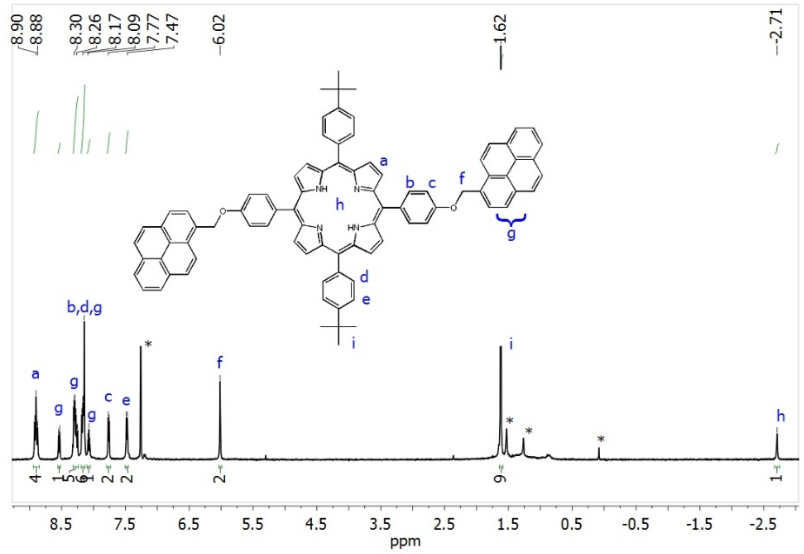

Figure 17. ^{1}H NMR of Porphyrin **1b** in $CDCl_3$. All integrations are halved due to molecular symmetry.

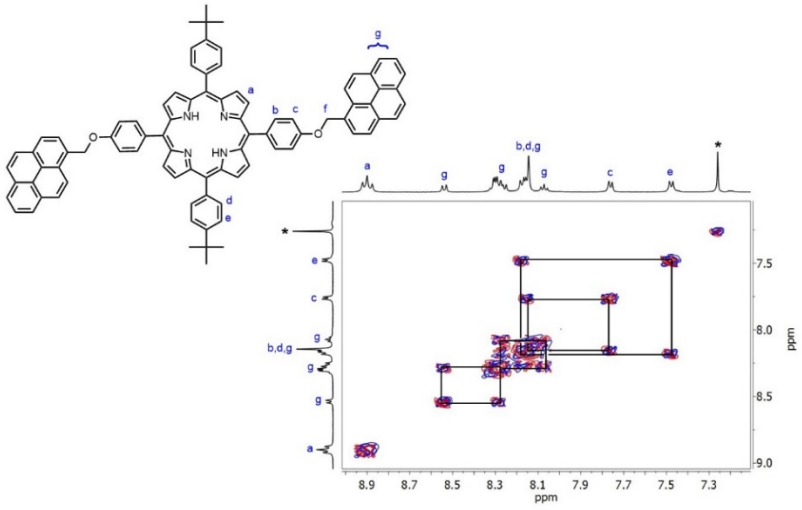

Figure 18. COSY NMR of Porphyrin **1b** in $CDCl_3$. Asterisks represent solvent impurities.

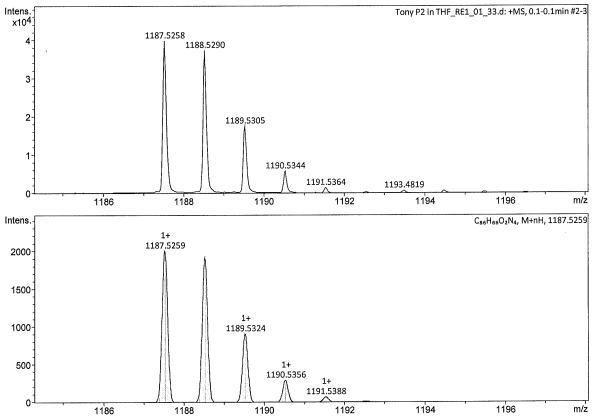

Figure 19. HRMS of porphyrin **1b**. Experimental spectrum at top, predicted spectrum at bottom.

Porphyrin **2a** (Figures 20-21). The ^{1}H NMR (Figure 20) and HRMS (Figure 21) indicate the successful synthesis and purification of porphyrin **2a**. The NH signals appear highly shielded and upfield (-1.12 ppm) which is typical for porphyrins due to the diatropic ring current.[45,63] furthermore, the integration of signals display a 3:1 substitution of ferrocene to pyrene. The experimental HRMS matches the theoretical isotope abundance and molecular ion peaks.

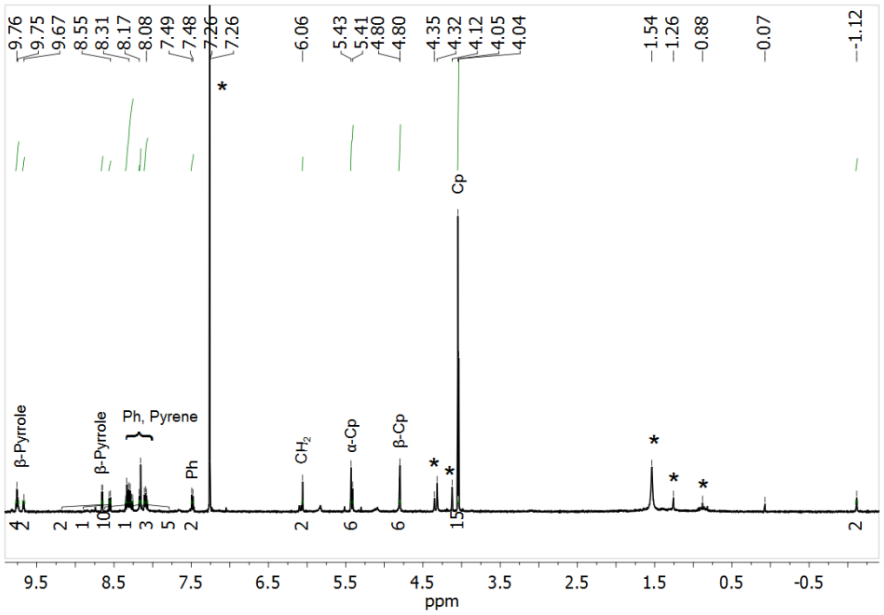

Figure 20. ^{1}H NMR of porphyrin **2a** in $CDCl_3$.

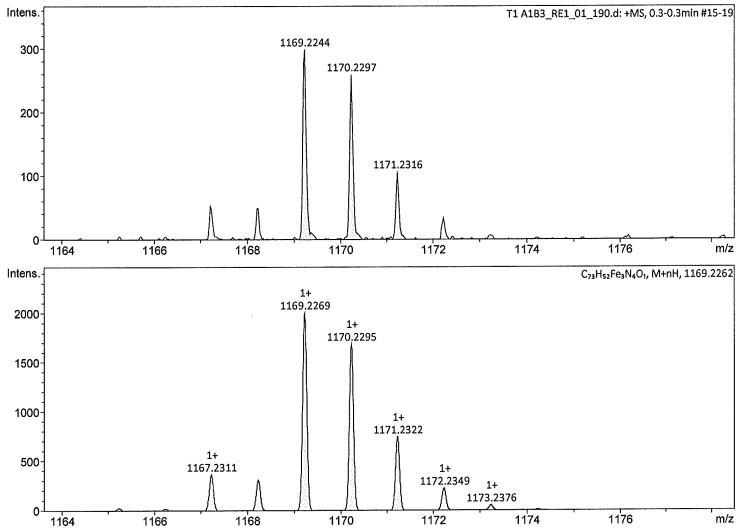

Figure 21. Mass spectrum of porphyrin **2a**. Experimental spectrum at top, predicted spectrum at bottom.

Porphyrin **2b** (Figures 22-24). The ^{1}H NMR (Figure 22) and COSY NMR (Figure 23) indicate the successful synthesis and purification of porphyrin **2b**. The NH signals appear highly shielded and upfield (-1.62 ppm) which is typical for porphyrins due to the diatropic ring current.[45,63] Furthermore, the integration of signals display a 2:2

substitution of ferrocene to pyrene. Since bulky ferrocene groups cause nonplanarity of the porphyrin core, the distinct NH signal indicates the *trans* isomer.[63] The *cis* isomer provides an NH signal at -1.77 ppm (Supplementary Information, Figure S4). The HRMS of target porphyrin **2b** (Figure 24) shows excellent agreement with the predicted spectra and isotope abundances.

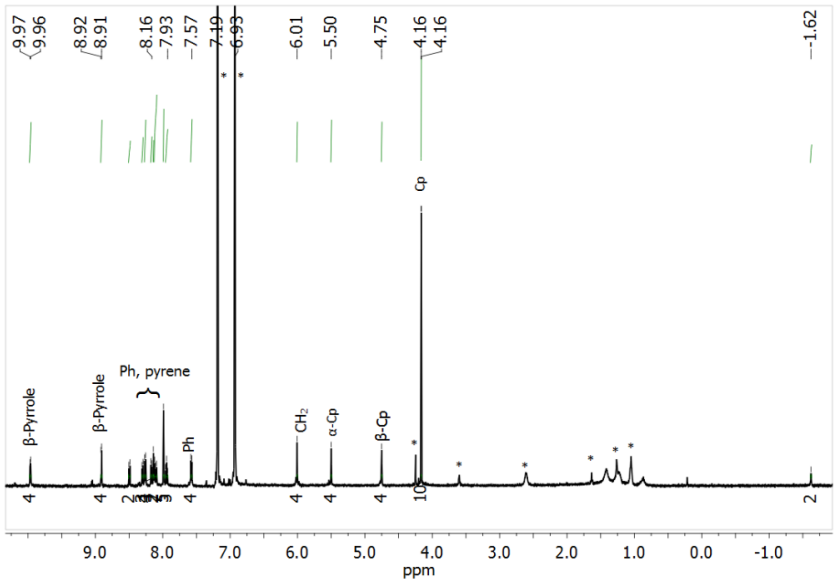

Figure 22. ^{1}H NMR of porphyrin **2b** in *o*-DCB.

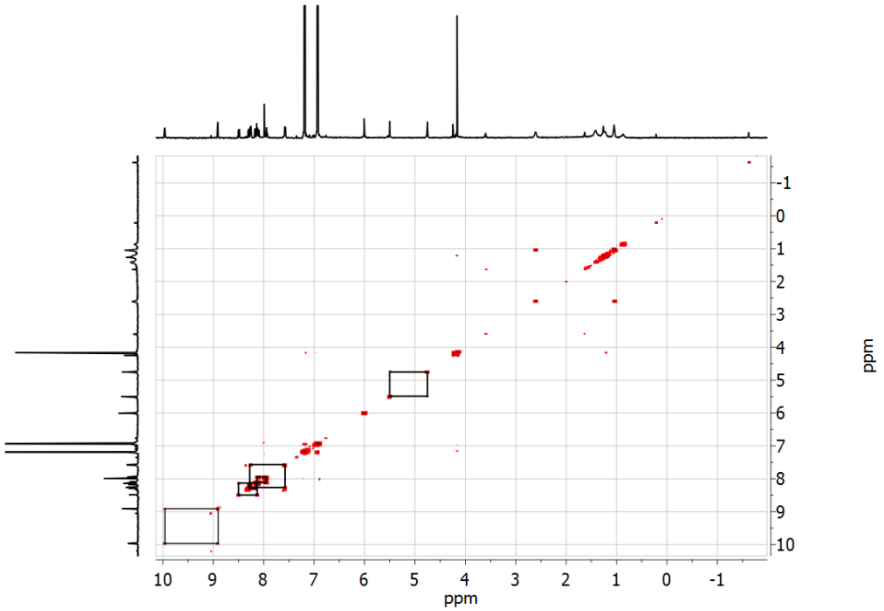

Figure 23. COSY NMR of Porphyrin **2b** in *o*-DCB.

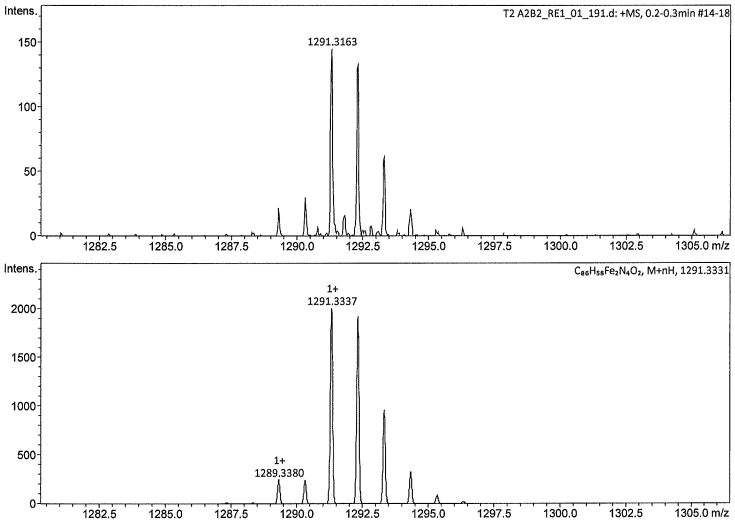

Figure 24. Mass spectrum of porphyrin **2b**. Experimental spectrum at top, predicted spectrum at bottom.

3.3. UV-Vis-NIR Spectroscopy

Typically, the UV-Vis spectra of porphyrin can be characterized by two absorption regions. The first absorption region is the Soret band (sometimes referred to as the *B*-band), which is a sharp and intense absorption near 420 nm, typically on the scale of 10^5 $M^{-1}cm^{-1}$. The second absorption region is typically between 500 and 750 nm and labelled as the *Q*-bands. These transitions are much lower in intensity, between 10^2 and 10^4 $M^{-1}cm^{-1}$. Also seen in the UV-Vis spectrum of these specific porphyrins are the characteristic absorption bands of pyrene between 300 and 350 nm.

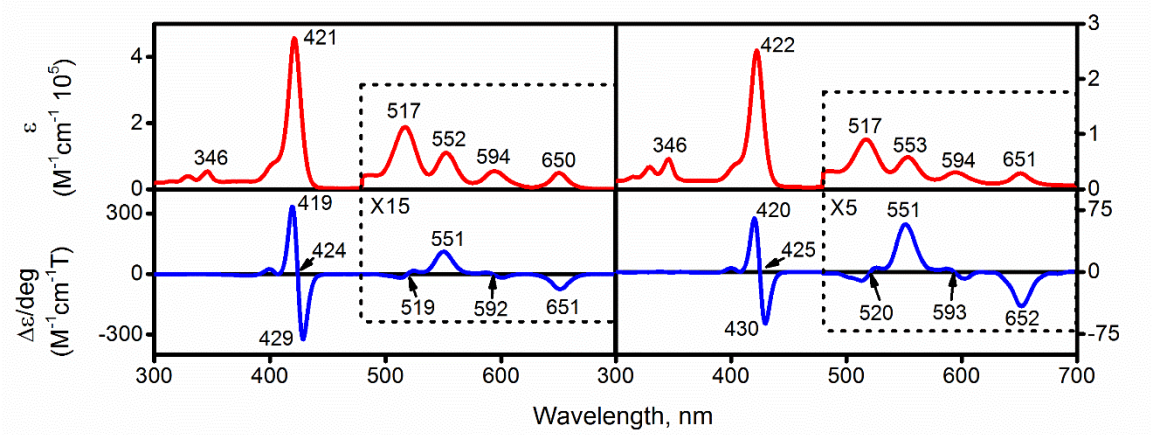

Figure 25. UV-Vis (top) and MCD (bottom) spectra of porphyrins **1a** (left) and **1b** (right).

Porphyrins **1a** and **1b** have almost identical absorption and MCD spectra (Figure 25). They each exhibit an intense optical transition near 420nm (Soret band) and low intensity transitions between 450 and 700 nm (*Q*-bands). In the UV-Vis and MCD spectra, the *Q*-bands consist of four distinct signals, which are attributed to $S_0 \rightarrow S_1$ transitions at different vibronic levels. From low to high energy, the transitions are $Q_{0\text{-}0}(x)$, $Q_{0\text{-}1}(x)$, $Q_{0\text{-}0}(y)$, and $Q_{0\text{-}1}(y)$ whereas 0-0 represents $S_0 \rightarrow S_1$ lowest vibronic energy level and 0-1 represents $S_0 \rightarrow S_1$ first vibronic energy level. From low to high energy, the MCD transitions are alternating, negative to positive, in nature. Since D_{2h} effective symmetry for porphyrins **1a** and **1b** forbids degeneracy in the lowest unoccupied molecular orbital (LUMO), these transitions must have predominant contribution from the single-electron excitation of the highest unoccupied molecular orbital (HOMO) to LUMO and HOMO to LUMO+1, which are similar in energy but not in electronic structure, which will be discussed more in depth later in this thesis.

The Soret band, which arises from the $S_0 \rightarrow S_2$ transitions, is extremely intense in the UV-Vis spectrum and is represented by a pseudo Faraday A-term on the MCD

spectrum for each porphyrin. The pseudo A-term is the result of an overlap between two B-terms caused by the HOMO-1 to LUMO and HOMO-1 to LUMO+1 electronic transitions.

The pyrene absorptions, with maxima at 328 nm and 346 nm, show expected low intensities on the MCD spectra.

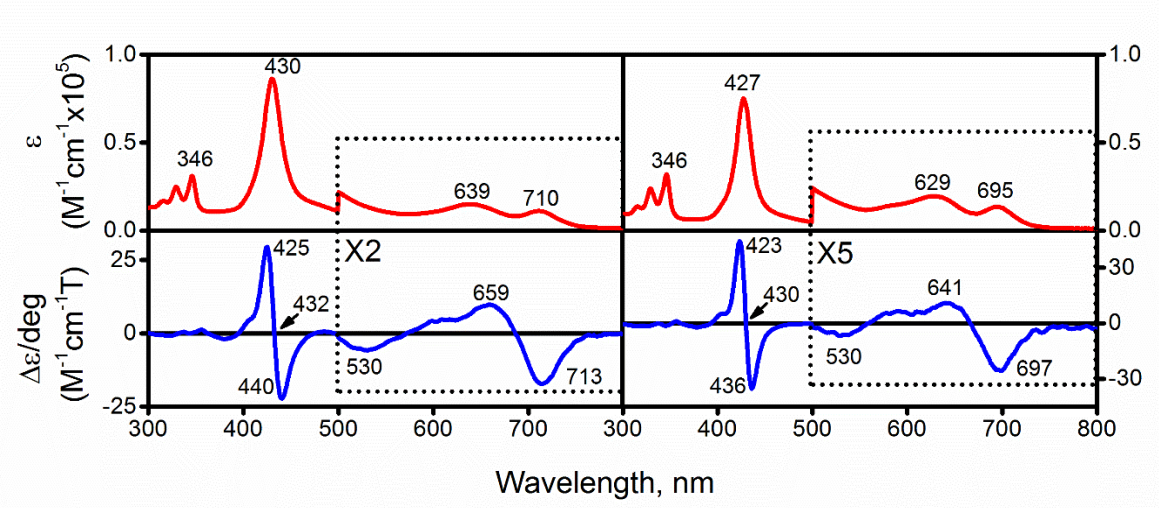

Figure 26. UV-Vis (top) and MCD (bottom) spectra of porphyrins **2a** (left) and **2b** (right).

The ferrocenyl porphyrins (**2a** and **2b**) show a broadening and red-shift of the Soret band as compared to porphyrins **1a** and **1b**, which is characteristic of ferrocenyl porphyrins (Figure 26).[63] The decrease in molar absorbance and red-shift are attributed to a decrease in the π-orbital overlap caused by a decrease in planarity of the porphyrin core.[63] This claim is further supported by deshielding seen in the chemical shifts of the NH signals observed in the ^{1}H NMR spectra.

The ferrocenyl porphyrins display a similar MCD pattern to porphyrins **1a** and **1b**, with the exception of the easily visible $Q_{0\text{-}1}$(x) and $Q_{0\text{-}1}$(y) transitions. From low to

higher energy, there is a negative B-term from the *Q*(x) transitions and a positive B-term from the *Q*(y) transitions, which are typical for *meso*-substituted porphyrins.[63]

3.4. DFT and TDDFT Calculations

The DFT optimized structures for porphyrins **1a** and **1b** were found to be almost completely planar from a qualitative interpretation (Figure 27). However, porphyrins **2a** and **2b** showed deviations from planarity with **2a** being more nonplanar than **2b**, which further supports earlier claims seen by NMR, UV-Vis, and MCD spectroscopy.

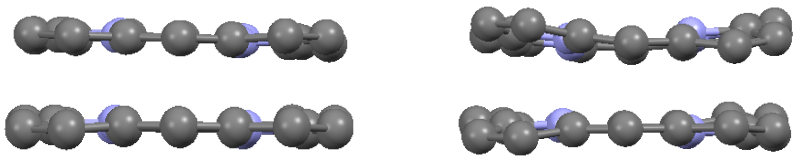

Figure 27. Side view of the DFT optimized structures of porphyrin cores of **1a** (top, left), **1b** (bottom, left), **2a** (top, right) and **2b** (bottom, right). For simplicity, only the porphyrin core is shown.

The single point energy calculations allow an in-depth analysis of the electronic structure of each optimized porphyrin molecule. Complete analysis of the optimized structures and single point energies can be found in the Supporting Information. Energy levels of each porphyrin are shown in Figure 28. The HOMO-LUMO difference, or band gap, decreases slightly for the ferrocene derivatives relative to porphyrins **1a** and **1b**. Furthermore, the LUMO and LUMO+1 for porphyrins **1a** and **1b** appear to be accidentally degenerate in energy, but their effective D_{2h} symmetry forbids degeneracy. This can be seen in both the frontier orbital images and molecular orbital composition diagrams (Figures 29-31). The LUMO and LUMO+1 for porphyrins **2a** and **2b** is clearly split due to the decreased effective symmetry.

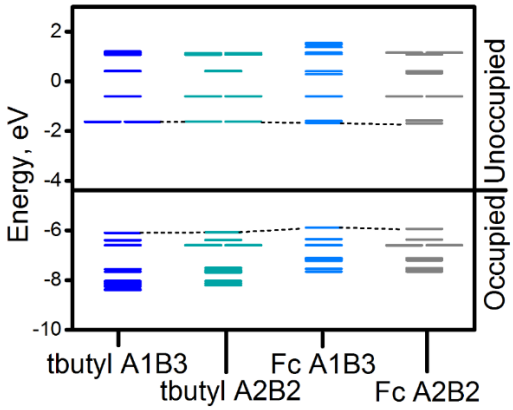

Figure 28. Frontier orbital energy diagram for porphyrins **1a** (tbutyl A1B3), **1b** (tbutyl A2B2), **2a** (Fc A1B3), and **2b** (Fc A2B2).

The molecular orbital compositions, TDDFT predicted UV-Vis spectra, experimental UV-Vis spectra, and frontier orbital images can be seen in Figures 29-34. Porphyrins **1a** and **1b** show a HOMO→LUMO transition that is predominately a porphyrin-centered, π-π transition. Pyrene transitions do not appear to interact with the electronic structure of the porphyrin core, suggesting that pyrene acts as a separate chromophore. Electronic transitions involving pyrene are predominately pyrene-localized, π-π transitions, with very minor contribution from the porphyrin core. Transitions in the *Q*-band region in both **1a** and **1b** are a combination of the HOMO→LUMO, HOMO→LUMO+1, HOMO-1→LUMO, and HOMO-1→LUMO+1 single electron excitations, which are predominately porphyrin-centered, π→π in nature. The Soret band transitions are predominantly porphyrin π-centered HOMO-1→LUMO and HOMO-1→LUMO+1 transitions. Likewise, the *Q*-band transitions and Soret transitions in porphyrins **2a** and **2b** are identical to that of porphyrins **1a** and **1b**. Unlike porphyrins **1a** and **1b**, porphyrins **2a** and **2b** show evidence of charge transfer with transitions of HOMO-3→LUMO+1, HOMO-4 →LUMO and HOMO-4→LUMO,

HOMO-5→LUMO, respectively, from ferrocene centered to porphyrin centered electronic transitions. In both situations the calculated energy of the metal to ligand charge transfer (MLCT) is near 4 eV. The computational methods used largely overestimate the interaction energy of the ferrocene d-orbitals with the π-orbitals of the porphyrin core. However, it is known experimentally that ferrocenyl porphyrins exhibit a MLCT near 1.5 eV.[63] Experimentally we were not able to see these intensities in the UV-Vis spectra, possibly due to their low molar absorption coefficients. However, fluorescence experiments may provide more information on possible charge transfer.

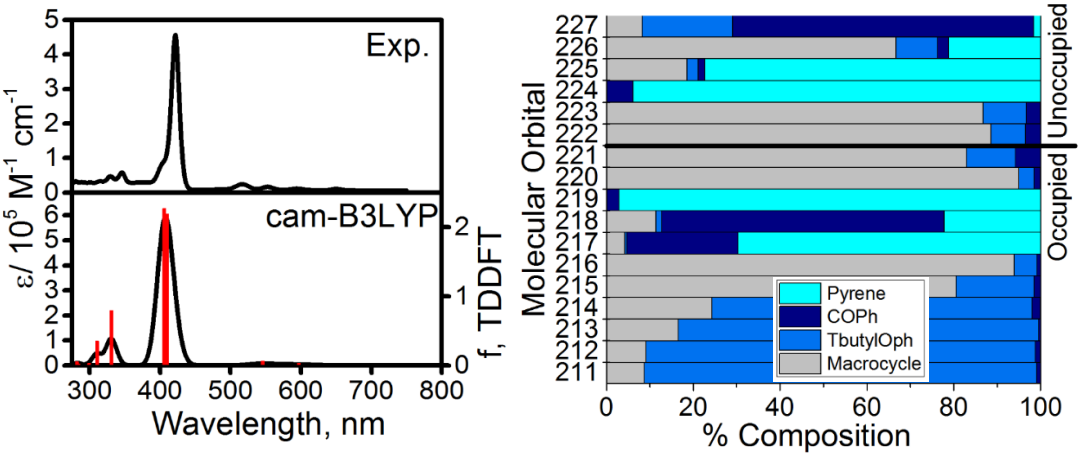

Figure 29. Experimental (left, top), TDDFT-predicted (left, bottom) spectra and molecular orbital composition diagram (right) of porphyrin **1a**.

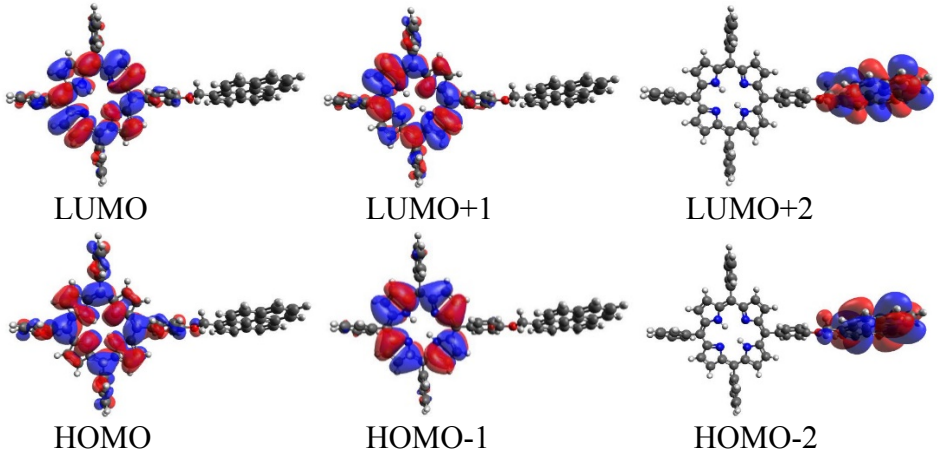

Figure 30. Frontier orbitals of porphyrin **1a**.

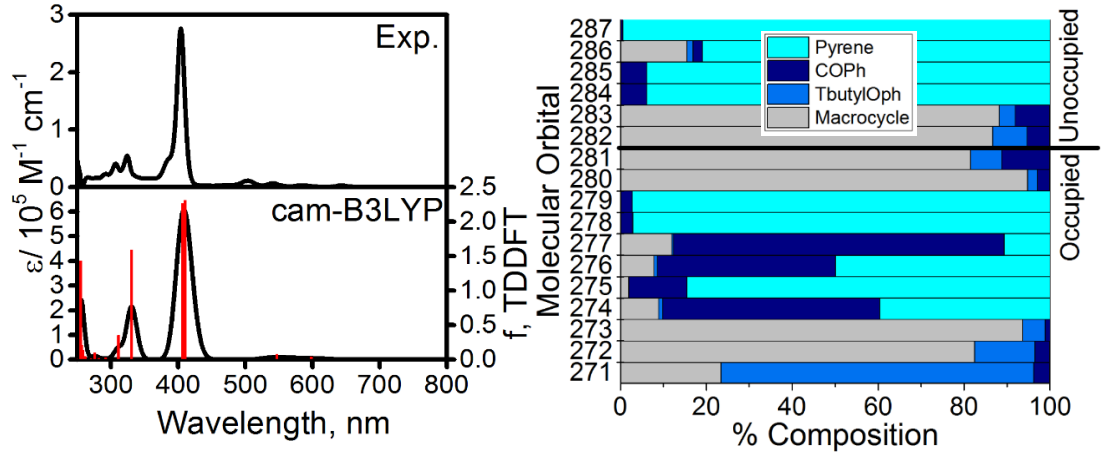

Figure 31. Experimental (left, top), TDDFT-predicted (left, bottom) spectra and molecular orbital composition diagram (right) of porphyrin **1b**.

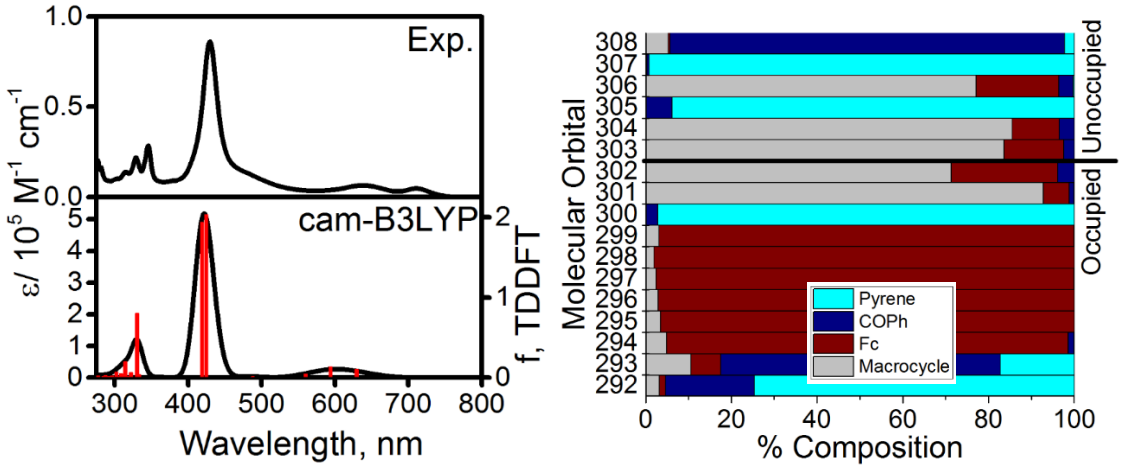

Figure 32. Experimental (left, top), TDDFT-predicted (left, bottom) spectra and molecule orbital composition diagram (right) of porphyrin **2a**.

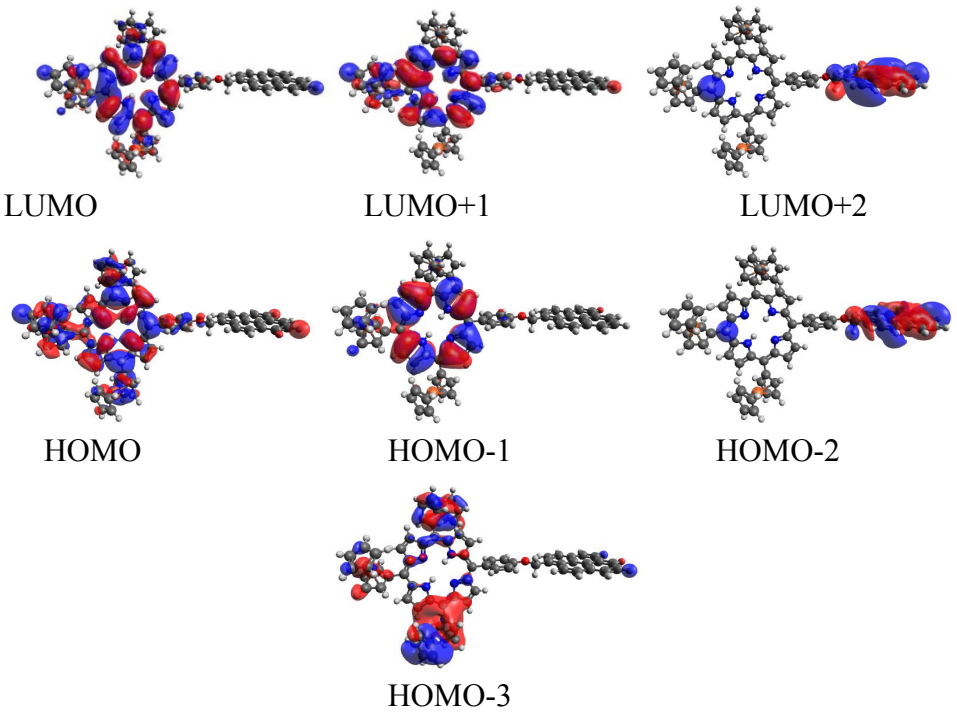

Figure 33. Frontier orbitals of porphyrin **2a**.

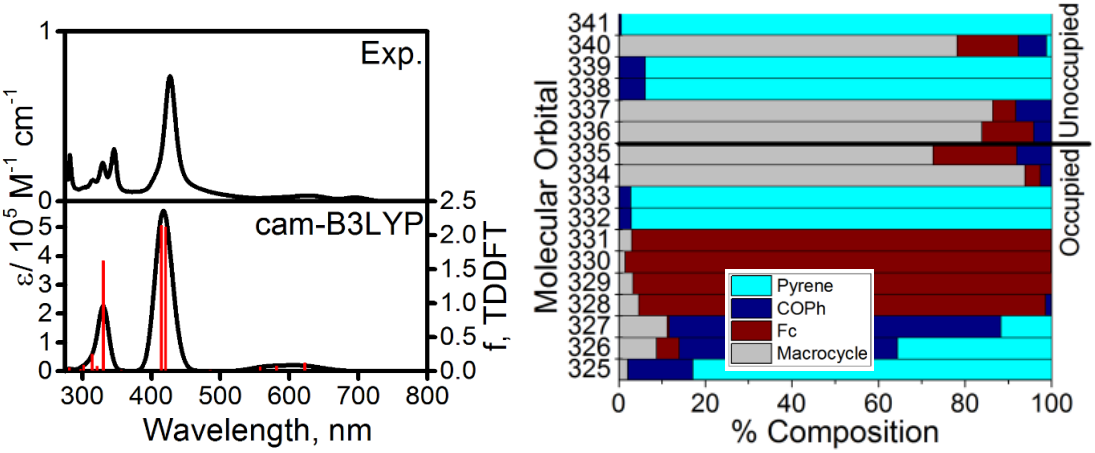

Figure 34. Experimental (left, top), TDDFT-predicted (left, bottom) spectra and molecule orbital composition diagram (right) of porphyrin **2b**.

3.5. Steady-State Fluorescence

As a compliment to absorption spectroscopy, fluorescence provides information of where and how molecules react to incident photons.[10] Fluorescence works in a very simple fashion; a solution is excited by incident photons, the excited electrons can follow

one of three main deactivation pathways. First, electrons can deactivate nonradiatively, in which the electron relaxes back to the ground state without any luminescence.[10] Second, electrons and undergo fluorescence, in which the excited electron relaxes to the lowest vibrational level and then emits a photon as it relaxes to the ground state. In addition, excited electrons have the ability to undergo internal conversion, which they nonradiatively relax to a lower excited electronic state and then can fluoresce from there.[10] This process is displayed in Figure 35 as a transition from S_2 to S_1 followed by fluorescence from S_1 to S_0. Finally, electrons can undergo phosphorescence in which the electron undergoes a spin flip via an intersystem crossing mechanism and then returns to its original spin direction and relaxes to the ground state.[10]

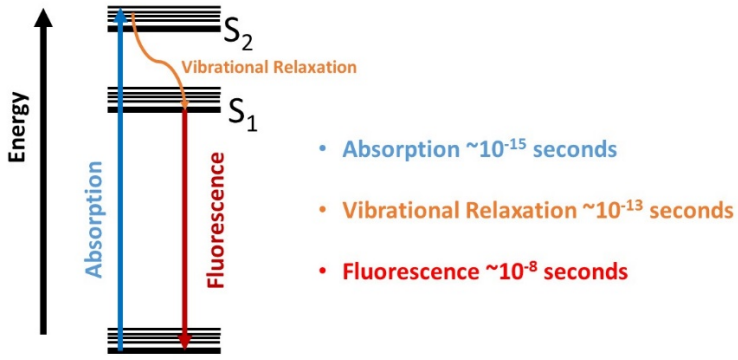

Figure 35. Jablonski diagram of absorbance and fluorescence. S_n and large horizontal lines denote energy states, small horizontal lines represent vibronic energy levels.

Since fluorescence spectroscopy is extremely sensitive to fluorescent impurities, extra caution was used to ensure the high purity of each molecule as well as the solvent used.[10] Fluorescence measurements were recorded for porphyrin solutions with Abs(Soret) ≈ 0.5 in freshly distilled dry toluene. It was observed that porphyrins **1a** and **1b** exhibited significant fluorescence when excited at both 328 nm (Figure 36) and their respective Soret bands. A residual pyrene fluorescence is seen near 390 nm while

porphyrin fluorescence is intense near 650 nm and 720 nm.

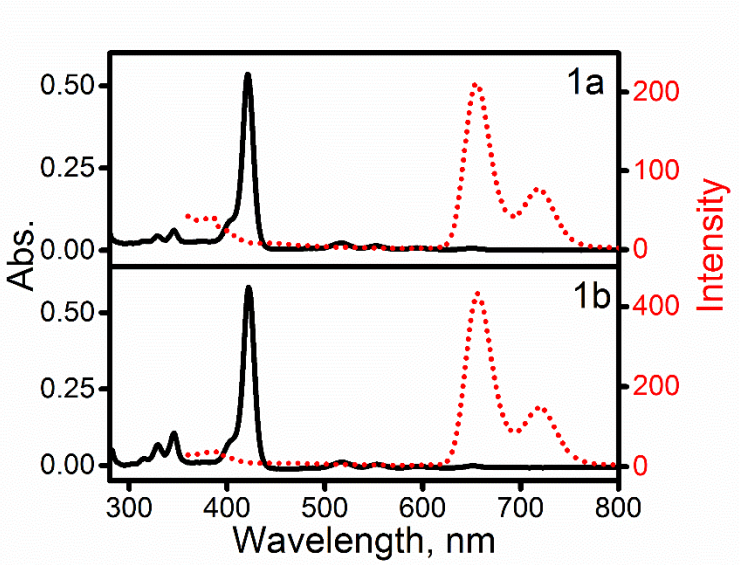

Figure 36. Absorbance (black, solid) and fluorescence (red, dotted) spectral overlays for porphyrin **1a** (top) and porphyrin **1b** (bottom) in toluene. Excitation was recorded using 328nm excitation, excitation and emission slits of 20 nm each.

Unlike porphyrins **1a** and **1b**, porphyrins **2a** and **2b** show little to no porphyrin fluorescence but do possess some residual fluorescence from pyrene (Figure 37). The absence of porphyrin fluorescence indicates that there is an intramolecular quenching process occurring when the porphyrin is in an excited state. Since ferrocene has a strong ability to donate electrons and possess a stable Fe^{3+} oxidation state, it is most probable that ferrocene undergoes electron transfer to the vacant porphyrin ground state, preventing fluorescence from occurring.[64–66] This claim is supported by the evidence of a metal to ligand charge transfer observed from TDDFT calculations.

One process that is clearly prominent in each of the pyrene-bearing porphyrins is the process of fluorescence resonance energy transfer (FRET). Although it is a qualitative observation, literature quantum yields for pyrene (ϕ_f=0.61)[67] and H_2TPP (ϕ_f=0.11)[68] suggest that pyrene should show much greater fluorescence than porphyrin when excited

at 328 nm whereas pyrene's molar absorption is roughly double than that of H_2TPP. Furthermore, porphyrins have molar absorption coefficients near $3.5x10^4$ $M^{-1}cm^{-1}$ at 395 nm (where pyrene fluorescence is most intense) suggesting that the porphyrins can easily absorb the emitted energy from the excited pyrene. FRET has been studied on similar molecules and shown to be a very prominent photophysical process.[69,70]

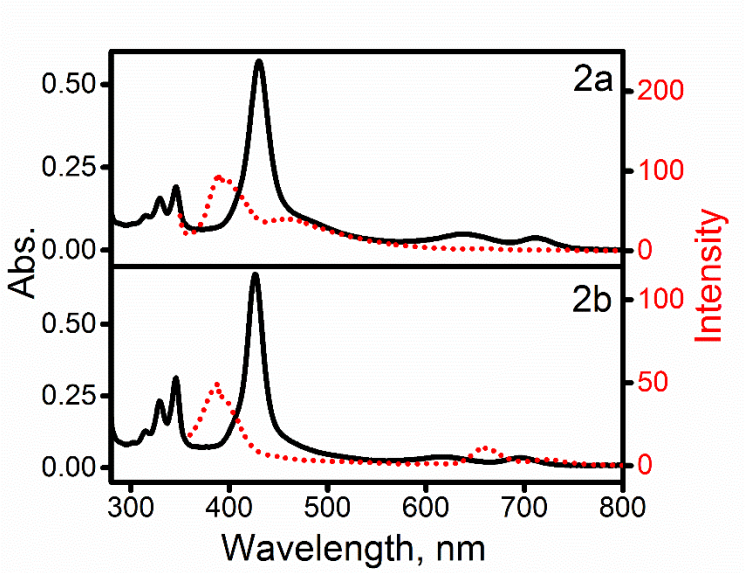

Figure 37. Absorbance (black, solid) and fluorescence (red, dotted) spectral overlays for porphyrin **2a** (top) and porphyrin **2b** (bottom) in toluene. Excitation was recorded using 328nm excitation, excitation and emission slits of 20 nm each.

3.6. Interactions with C_{60} Fullerene

In order to investigate the intermolecular interactions with C_{60}, several incremental additions of C_{60} solution in toluene were added (0 to 10 equivalents) to porphyrin solutions and both absorbance and fluorescence were recorded. If intermolecular interactions are very strong, a ground state complex may form and be seen in the absorbance spectra. It is almost certain that electron transfer is possible if a ground state complex is formed.[46,47,71] In the fluorescence spectra, it is expected that C_{60} will

quench the porphyrin fluorescence but whether it is through energy or electron transfer is a question we hope to address.

All UV-Vis and fluorescence spectra were corrected for dilution factors. Fluorescence spectra were further corrected for competitive absorption of C_{60} using the following equation[72]:

$$I_{corr} = I\left(\frac{1-e^{-\varepsilon_a C_a}}{\varepsilon_a C_a}\right)\left(\frac{\varepsilon_a C_a + \varepsilon_b C_b}{1-e^{-(\varepsilon_a C_a + \varepsilon_b C_b)}}\right)\left(\frac{\varepsilon(em)_b C_b}{1-e^{-\varepsilon(em)_b C_b}}\right)$$

Where I_{corr} is the corrected fluorescence. ε_a and ε_b are the molar absorption coefficients of the fluorophore (porphyrin) and C_{60}, respectively, at the excitation wavelength. $\varepsilon(em)_b$ is the molar absorption coefficient of C_{60} at the emission wavelength. C_a and C_b are the concentrations of fluorophore and C_{60}, respectively.

Upon addition of C_{60} to the porphyrin solutions, a peak arises at 330 nm in the UV-Vis spectra (Figure 38-39). This peak is purely due to the absorption of C_{60}. In addition, slight increases in absorbance are observed from 440 to 650 nm, again, due to C_{60} absorption. It is unclear whether or not a ground state complex is formed. A constant Soret peak suggests that no complex is forming between the porphyrin core and C_{60}. It is difficult to see any such change in the pyrene absorption region due to the overwhelming absorbance of C_{60}. By taking the difference between the porphyrin absorbance and the absorbance after addition of C_{60}, only the C_{60} absorption was observed (Figure 39). Using a control experiment with molecule **5** being titrated with C_{60}, we did not observe any peak formation/deformation or isosbestic points. This suggest that a ground state complex between pyrene and C_{60} does not form, at least not in a large enough population to be seen by UV-Vis spectroscopy or that the C_{60} absorption is much more intense than the

molar absorbance of a ground state complex. Although the ground state complex cannot be observed via UV-Vis and in solution, it has been reported that similar systems have shown ground state complex formation in the solid phase.[73]

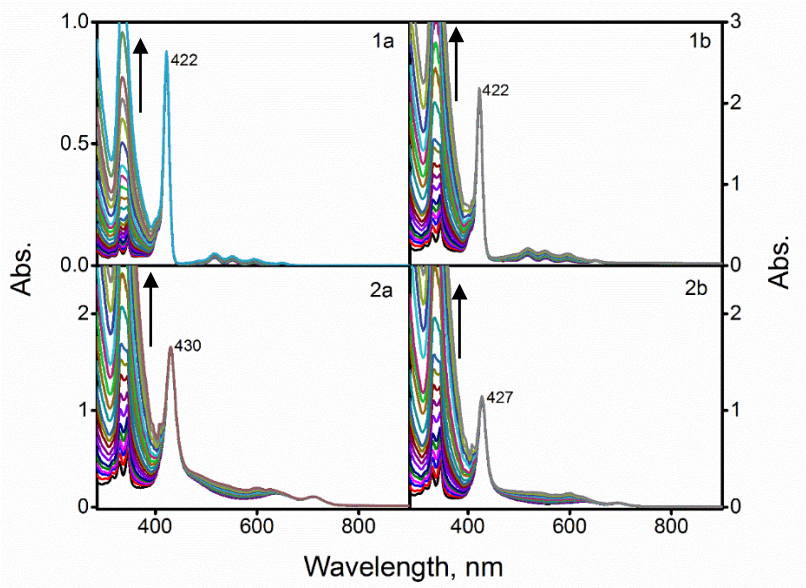

Figure 38. UV-Vis spectra of porphyrins **1a**, **1b**, **2a**, and **2b** (top left, top right, bottom left, and bottom right, respectively) with the addition of C_{60}.

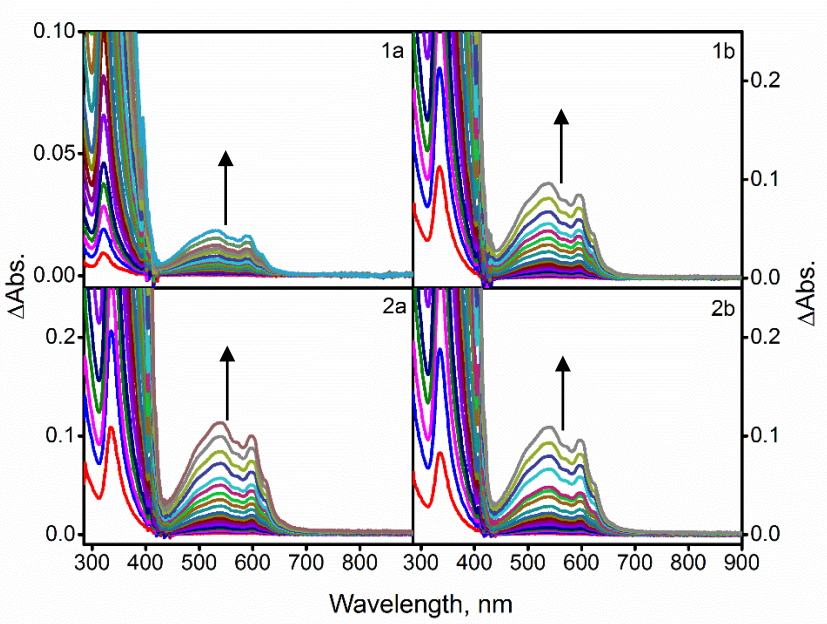

Figure 39. Difference UV-Vis spectra of **1a** (top, left), **1b** (top, right), **2a** (bottom, left), and **2b** (bottom, right).

Prior to testing the porphyrins, control experiments were conducted on molecule **5**, tetra-phenyl porphyrin (H_2TPP), and C_{60} to provide reference points. C_{60} did not display any fluorescence when excited at 328 nm or 420 nm. Both molecule **5** and H_2TPP exhibit significant fluorescence when excited at 328 nm (see Figure 40 and Figure 42, for the respective spectra).

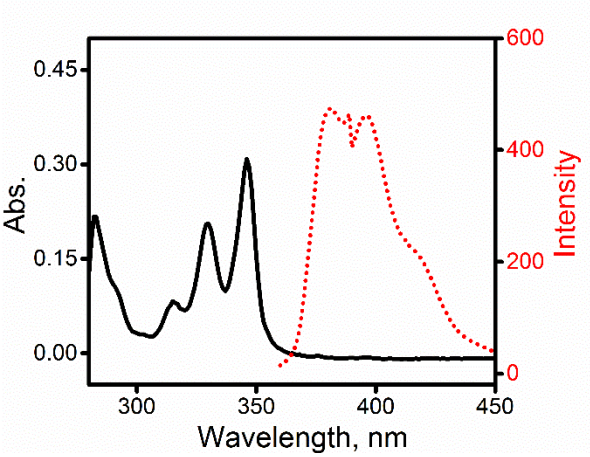

Figure 40. Absorbance (solid, black) and fluorescence (dotted, red) overlays of 1.5×10^{-5} M molecule **5** in toluene with excitation at 328 nm, excitation and emissions slit widths of 10 nm each.

Molecule **5** was titrated with C_{60} to provide an understanding of how C_{60} effects pyrene in the absence of porphyrin. It is observed that pyrene fluorescence is significantly quenched upon the addition of C_{60} (Figure 41). More interestingly is the change in linearity of the Stern-Volmer plot after 1 equivalent of C_{60} had been added. Although it is not possible to conclude what exactly causes this change from the steady-state fluorescence experiments, I have tentatively attributed it to a change in the diffusion dynamics in solution. Since pyrene has a large binding affinity to C_{60}, I suspect that C_{60} forms a long-lived encounter complex with pyrene while at the same time collisional quenching can occur from other C_{60} molecules. After one equivalent of C_{60} is added the

rate of quenching is halved due to quenching becoming primarily diffusion controlled. In addition C_{60} has a molar absorption of near 4100 $M^{-1}cm^{-1}$ at 395 nm, which allows the ability for FRET to occur, thus permitting nearby C_{60} molecules to quench the pyrene fluorescence.

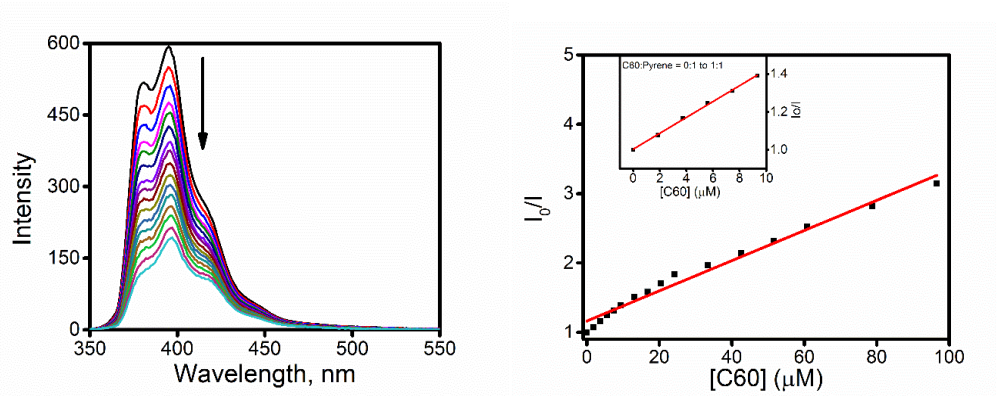

Figure 41. Fluorescence of molecule **5** upon addition of C_{60} (Left, excitation at 328nm). Stern-Volmer plot at 395nm (Right, inset is a linear fit between 0 and 1 parts C_{60} added).

Possible energetic pathways are outlined in equations 1-4, below. First, the pyrene excited state is populated by 328 nm photon (Equation 1). The excited electron can then follow one of three main pathways. First pathway the excited state simply returns to its ground state and emits a photon, or simply fluorescence (Equation 2). The second pathway is much more complex but consists of the formation of an encounter complex in which the donor (pyrene) and the acceptor (C_{60}) followed by electron transfer (Equation 3). The charged ions can either undergo back-transfer or decay back to their ground states via multiple routes. The third pathway is through FRET, in which energy is transferred via the formation of an encounter complex followed by energy transfer (Equation 4).

(1) $pyr + h\upsilon \rightarrow pyr^*$ Absorption

(2) $pyr^* \rightarrow pyr + f^*$ Fluorescence

(3) $pyr^* + C_{60} \rightarrow (pyr^{+\cdot} \cdots C_{60}{}^{-\cdot})$ Formation of encounter complex and electron transfer

(4) $(pyr^* \cdots C_{60}) \rightarrow pyr + C_{60}{}^*$ Formation of encounter complex and energy transfer

The porphyrin fluorescence is quenched at a steady rate for H_2TPP while quenching of porphyrins **1a** and **1b** are quenched in a more complex matter (Figures 42 and 43). From 0 to 2 equivalents of C_{60} added, fluorescence is quenched at approximately double the rate of quenching from 2 to 10 equivalents. Although the quenching process is simple in theory, the physical chemistry of it can be very complex. I have tentatively attributed the large degree of quenching at low molar equivalents to the favorability of pyrene to interact with C_{60}. This interaction will bring C_{60} close to the porphyrin core and thus have the ability to undergo both FRET with the excited pyrene and quench the excited porphyrin core. After 2 equivalents of C_{60}, the ability of the pyrenes to bind anymore C_{60} becomes greatly reduced due to sterics and the process becomes primarily diffusion controlled quenching like as in the case of molecule **5**. Since H_2TPP lacks any of the 'sticky' pyrene moieties, the quenching is strictly based on the diffusion of C_{60} into the Förster Radius of the porphyrins, which provides the nearly linear Stern-Volmer plot.

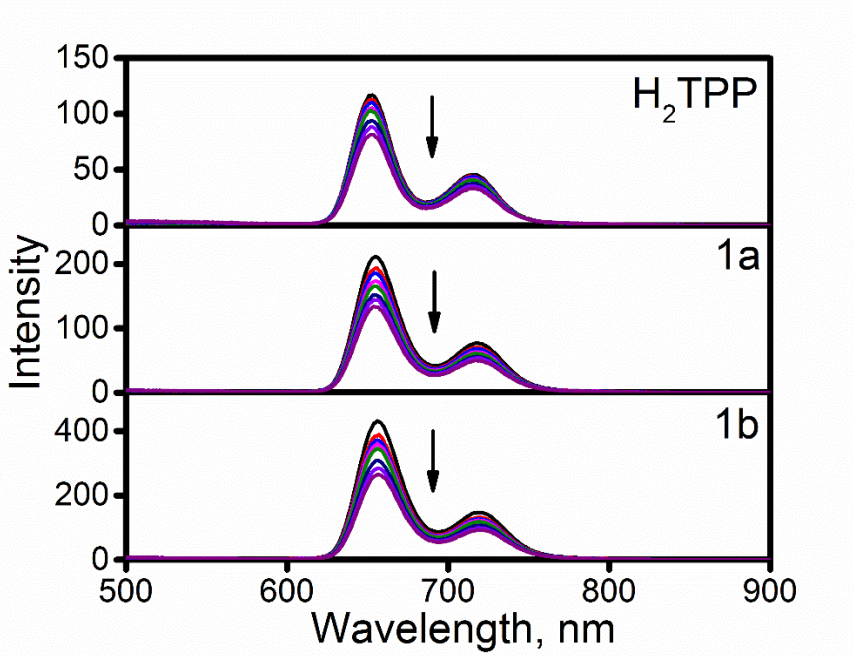

Figure 42. Fluorescence spectra of C_{60} additions to H_2TPP, porphyrin **1a** and porphyrin **1b**. Spectra were recorded using with excitation at 328 nm, excitation and emission slits at 20 nm.

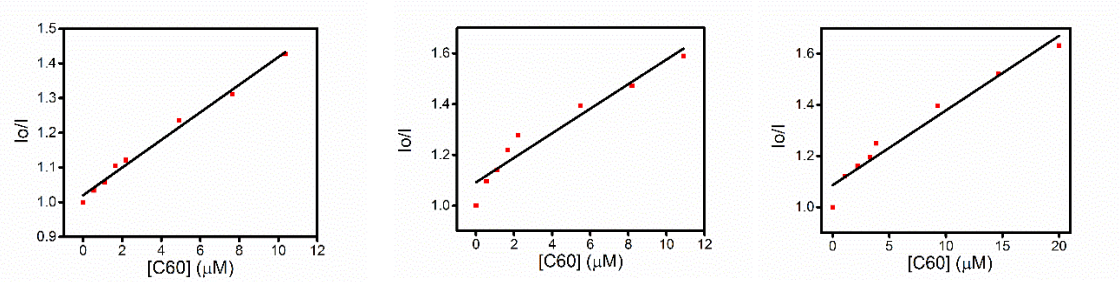

Figure 43. Stern-Volmer plots of H_2TPP (left), **1a** (middle), and **1b** (right) with excitation at 328 nm and emission at 652 nm, 655 nm, and 656 nm, respectively.

Upon excitation of the porphyrin Soret maximum, no appreciable decrease in fluorescence was observed when C_{60} was added to the porphyrin solutions (Figure 44). The absence of fluorescence quenching of the excited porphyrin core indicates that C_{60} lacks the ability to accept an electron and/or energy from the photoexcited porphyrin core. Furthermore, the lack of fluorescence quenching indicates that the quenching process when exciting the pyrene must be strictly between the pyrene and C_{60}, excluding

the porphyrin excited state. Since pyrene undergoes an electron and/or energy transfer with C_{60}, it can no longer undergo FRET with the porphyrin core thus a decrease in porphyrin fluorescence is observed. This explanation however does not provide a plausible reason why H_2TPP fluorescence is decrease upon the addition of C_{60}. Further photophysical experiments will need to be performed in order to provide a definite explanation to this phenomenon.

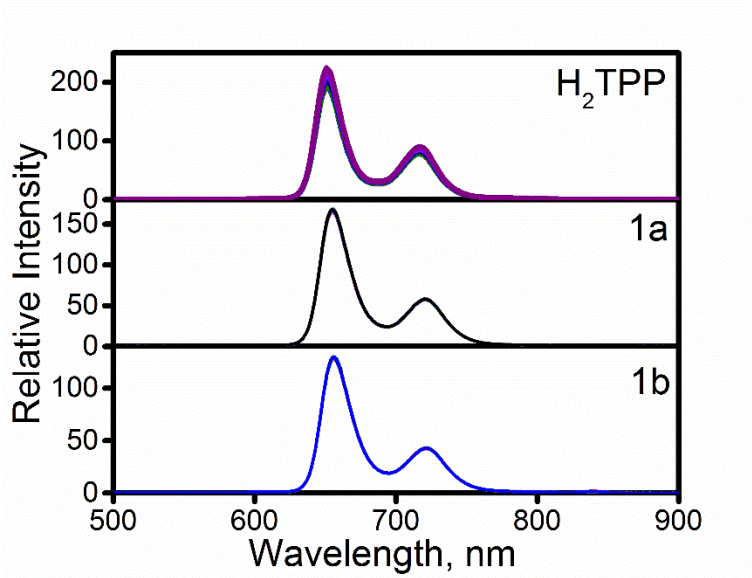

Figure 44. Fluorescence spectra of C_{60} additions to H_2TPP, porphyrin **1a** and porphyrin **1b**. Spectra were recorded with excitation at the respective Soret maxima, excitation and emission slits at 10 nm.

*3.7. Chemical Oxidation of Porphyrins **2a** and **2b***

Since porphyrins **2a** and **2b** do not exhibit significant fluorescence, titrations with C_{60} were not performed. It is well understood that the ferrocene substituents on the *meso* position quench the fluorescence of the excited porphyrin core by donating an electron to the porphyrin ground stated.[64–66] One way to determine if this is the situation is to oxidize the irons in the peripheral ferrocenes and record the fluorescence. In theory, if electron

donating ability of the irons is stripped away, then an increase in fluorescence should be observed.[65,66]

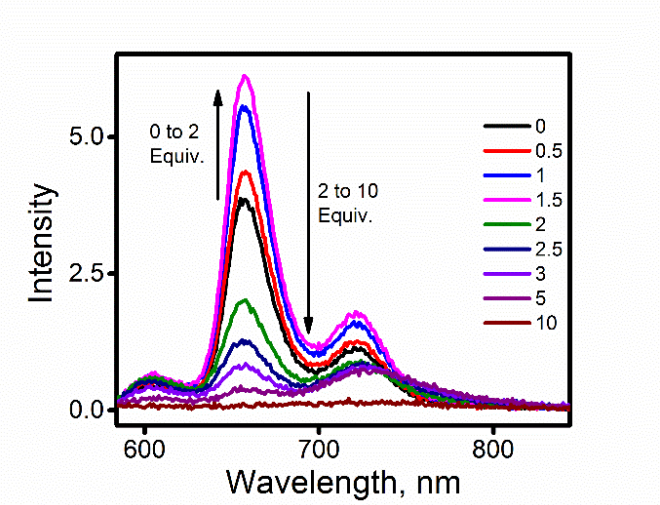

Figure 45. Fluorescence spectra of the chemical oxidation of **2b** with 0 to 10 equivalents of Magic Blue.

After oxidation with Magic Blue (Tris(4-bromophenyl)aminium hexa-chloridoantimonate), there was seen a slight increase in the porphyrin fluorescence until 2 equivalents were added (Figure 45). After 2 equivalents, fluorescence dramatically decreased until no fluorescence was observed at 10 equivalents. The low increase in fluorescence and quick decrease in all fluorescence suggests that the oxidant indiscriminately oxidizes both the ferrocenes and the porphyrin core. In addition, the UV-Vis spectra of before and after oxidation are dramatically different (Figure 46), further confirming that both the ferrocenes and porphyrin have been oxidized.

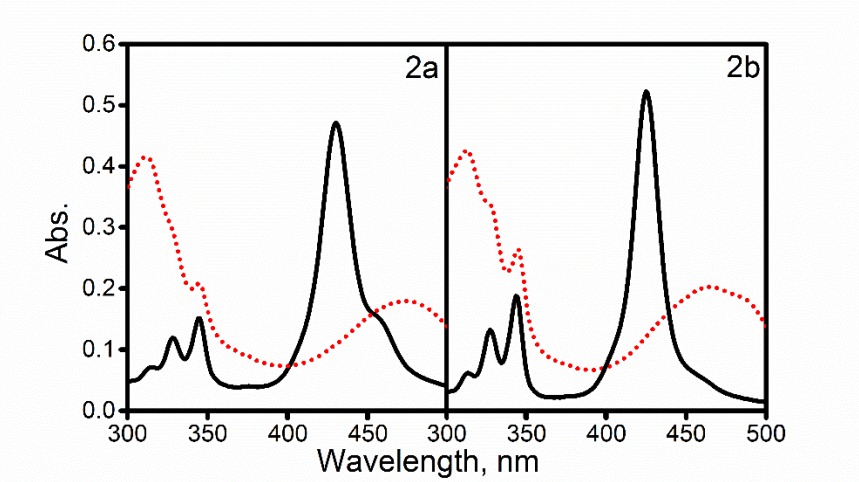

Figure 46. Oxidation of porphyrins **2a** and **2b** before (black, solid) and after (red, dotted) ten equivalents of oxidant, Magic Blue.

3.8. Transient Absorption Spectroscopy

The data presented here is under analysis by our photophysical chemist collaborator, Dr. David Blank, of the University of Minnesota. However, we do see significant differences in spectra upon the addition of C_{60}. Porphyrins **1a** and **1b** show an appearance of a peak near 950 nm after the addition of C_{60} (Figures 48 and 50, respectively). Porphyrins **2a** and **2b** show similar signature changes between 900 and 1050 nm (Figures 52 and 54, respectively)

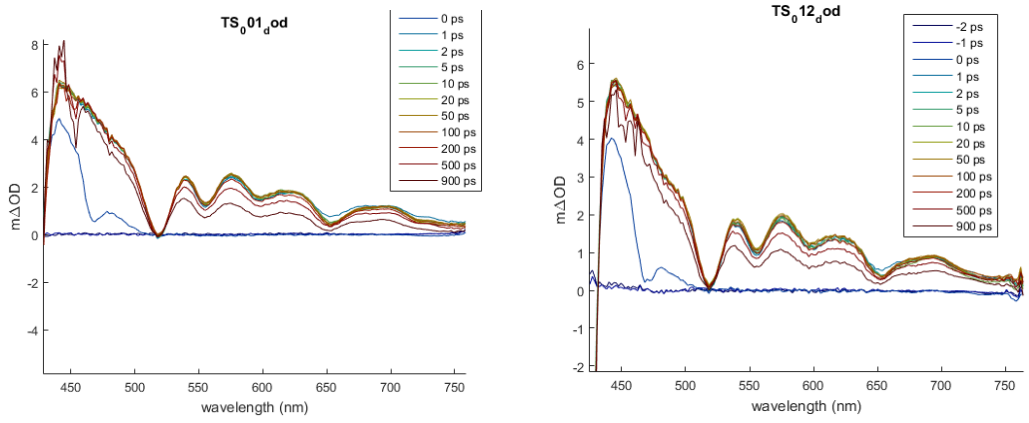

Figure 47. Vector scan of porphyrin **1a** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

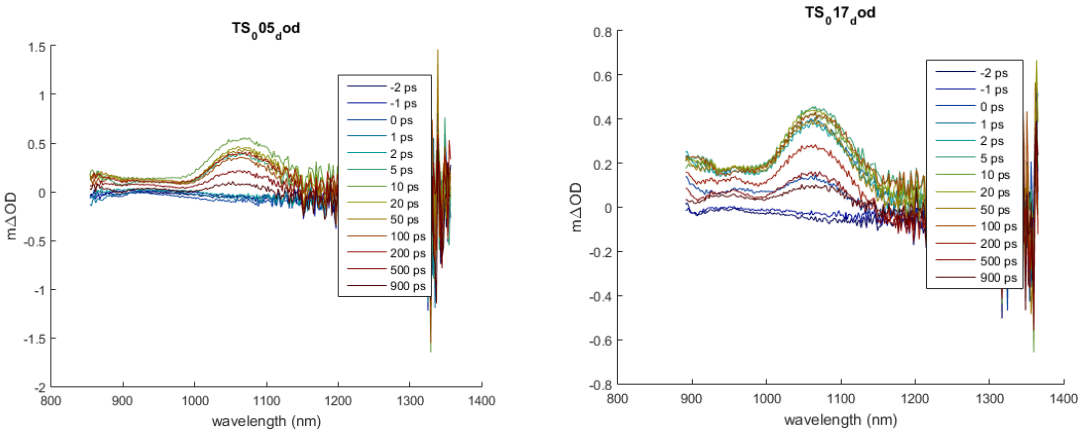

Figure 48. Vector scan of porphyrin **1a** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

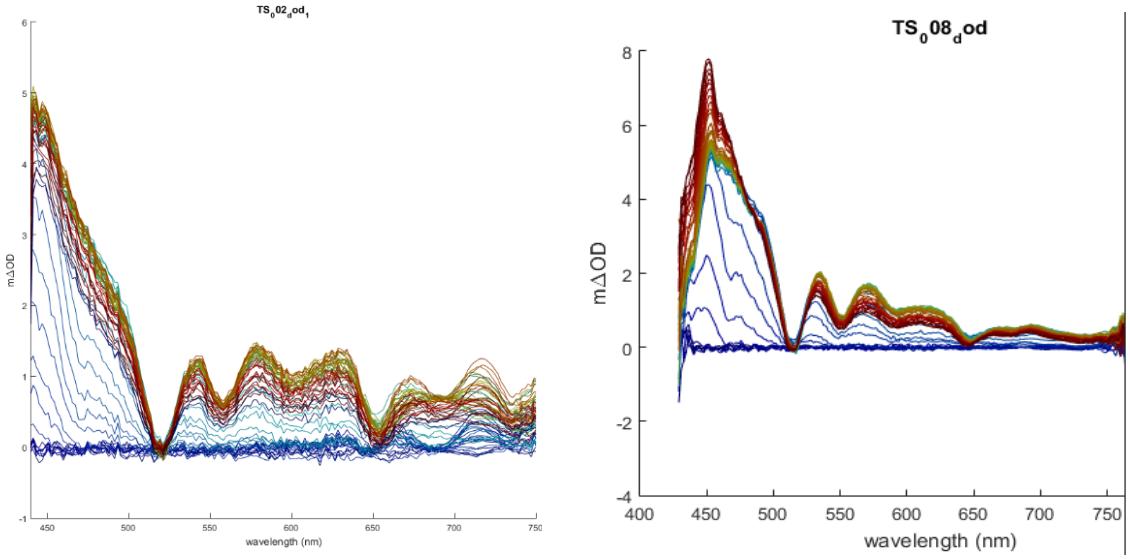

Figure 49. Array scan of porphyrin **1b** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

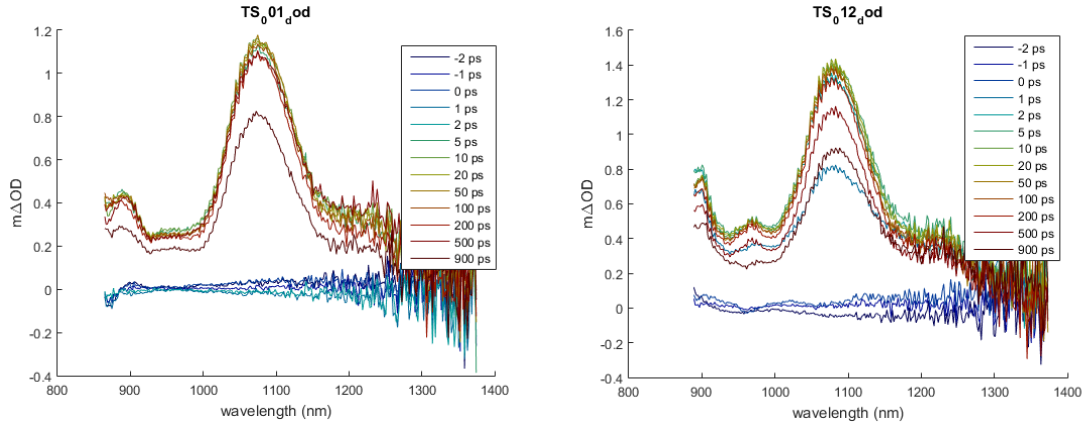

Figure 50. Vector scan of porphyrin **1b** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

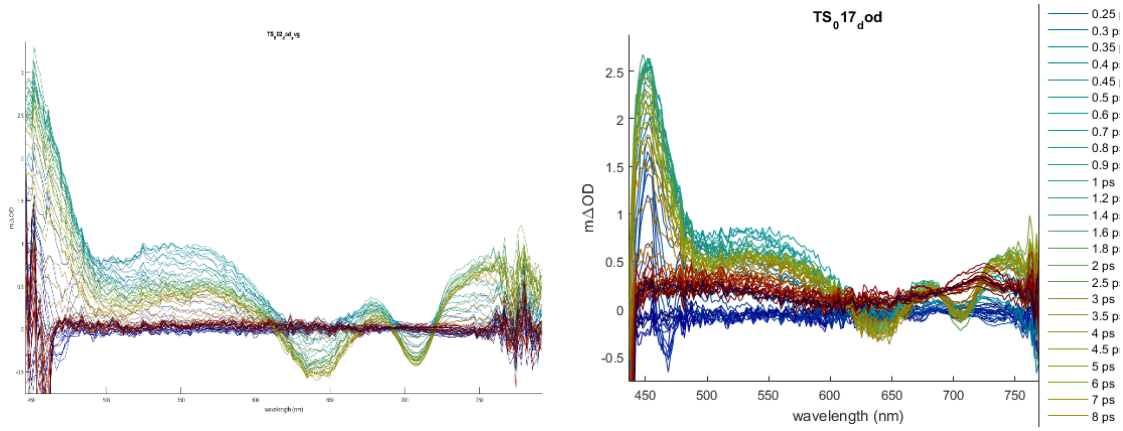

Figure 51. Array scan of porphyrin **2a** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

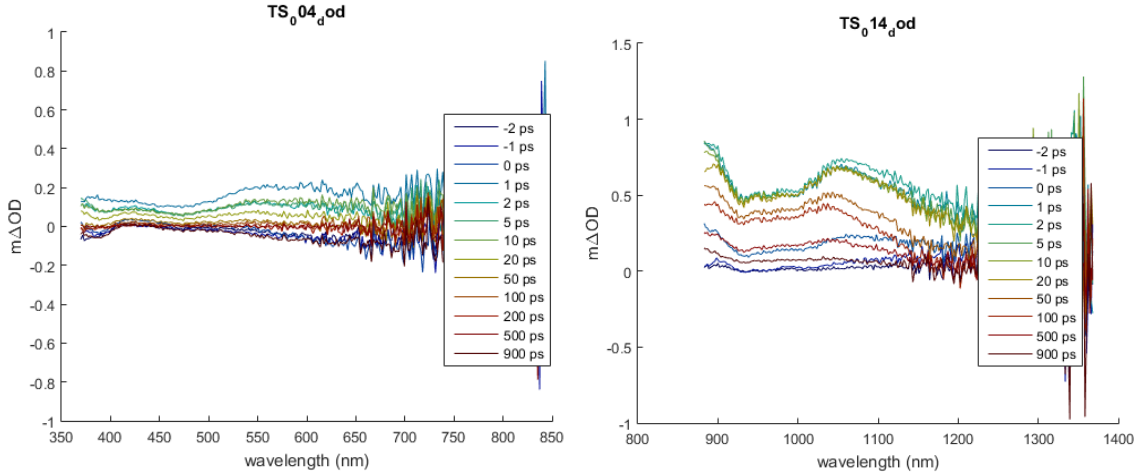

Figure 52. Vector scan of porphyrin **2a** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right). Axis are not correctly labelled.

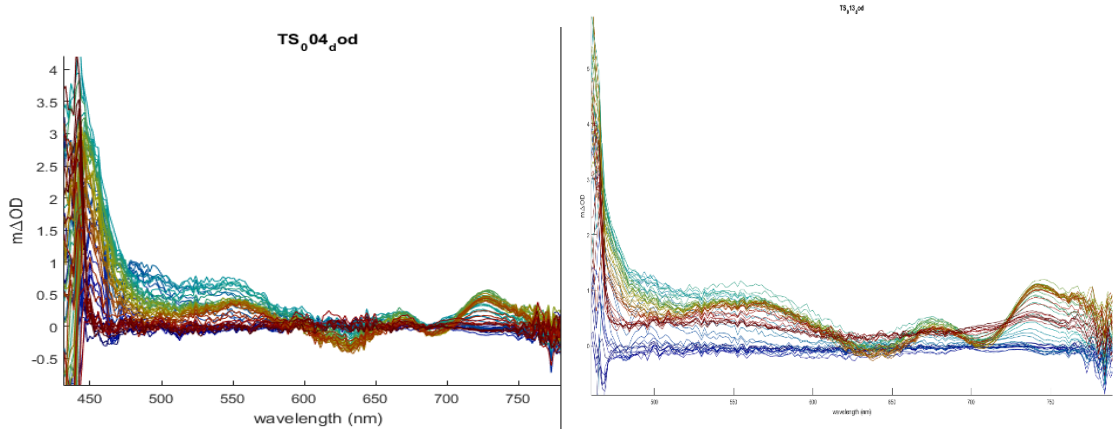

Figure 53. Array scan of porphyrin **2b** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right).

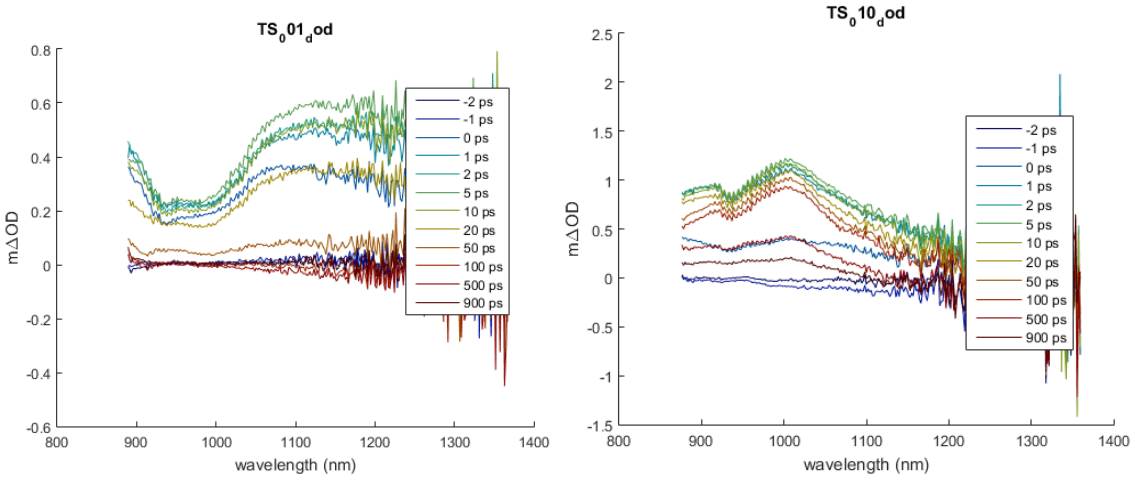

Figure 54. Vector scan of porphyrin **2b** in toluene without C_{60} (left) and with 5 equivalents C_{60} added (right). Axis are not correctly labelled.

Chapter 4 – Conclusion

Two different sets of novel pyrene-containing porphyrins were successfully synthesized and characterized via NMR, UV-Vis-NIR, MCD, FT-IR, fluorescence spectroscopy, and high-resolution mass spectrometry. The first set, which consisted of P_1B_3 and P_2B_2 porphyrins, was synthesized by the condensation of *t*-butylphenyl dipyrromethane (B) and newly reported 4-(1-pyrenylmethoxy)benzaldehyde (P). The second set consists of Fc_3P_1 and Fc_2P_2 porphyrins, which were synthesized by condensation of the dipyrromethane of the newly reported 4-(1-pyrenylmethoxy)benzaldehyde (P) and 1-ferrocenecarboxaldehyde (Fc).

UV-Vis spectroscopic studies led to inconclusive evidence of ground state formation between the target porphyrins and C_{60} fullerene mainly due to the overwhelming absorbance of C_{60}. However, fluorescence titrations of the target porphyrins with C_{60} indicate a strong interaction between the pyrene fragement(s) and C_{60}. A large decrease in fluorescence intensity was observed upon the addition of C_{60} to the porphyrin and pyrene solutions. Whether this interaction is due to energy or electron transfer is a question we hope to address upon complete analysis of the transient absorption spectroscopy experiments.

References

(1) US Census Bureau. *International Database*; 2015.
(2) British Petroleum. *BP Statistical Review of World Energy 2011*; 2011.
(3) Hansen, J.; Sato, M.; Ruedy, R. *J. Geophys. Res. Atmospheres* **1997**, *102* (D6), 6831–6864.
(4) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (43), 15729–15735.
(5) Kamat, P. V. *J. Phys. Chem. C* **2007**, *111* (7), 2834–2860.
(6) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2009**, *39* (1), 301–312.
(7) Kumar, B.; Kaushik, B. K.; Negi, Y. S. *Polym. Rev.* **2014**, *54* (1), 33–111.
(8) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492* (7428), 234–238.
(9) Jo, W.-K.; Tayade, R. J. *Ind. Eng. Chem. Res.* **2014**, *53* (6), 2073–2084.
(10) Skoog, D.; Holler, F. J.; Crouch, S. R. *Principles of Instrumental Analysis*, 6th ed.; Cengage.
(11) Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M. K.; Grätzel, M. *Thin Solid Films* **2008**, *516* (14), 4613–4619.
(12) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110* (11), 6595–6663.
(13) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33* (5), 269–277.
(14) Bierman, M. J.; Jin, S. *Energy Environ. Sci.* **2009**, *2* (10), 1050–1059.
(15) Wolden, C. A.; Kurtin, J.; Baxter, J. B.; Repins, I.; Shaheen, S. E.; Torvik, J. T.; Rockett, A. A.; Fthenakis, V. M.; Aydil, E. S. *J. Vac. Sci. Technol. A* **2011**, *29* (3), 030801.
(16) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353* (6346), 737–740.
(17) Grätzel, M. *Nature* **2001**, *414* (6861), 338–344.
(18) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Graetzel, M. *J. Am. Chem. Soc.* **1988**, *110* (4), 1216–1220.
(19) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. *Nat. Chem.* **2014**, *6* (3), 242–247.
(20) Urbani, M.; Grätzel, M.; Nazeeruddin, M. K.; Torres, T. *Chem. Rev.* **2014**, *114* (24), 12330–12396.
(21) Yella, A.; Mai, C.-L.; Zakeeruddin, S. M.; Chang, S.-N.; Hsieh, C.-H.; Yeh, C.-Y.; Grätzel, M. *Angew. Chem.* **2014**, *126* (11), 3017–3021.
(22) Man Gu Kang, K. M. *J. Electrochem. Soc.* **2004**, *151* (7).
(23) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18* (6), 789–794.
(24) Heeger, A. J. *Adv. Mater.* **2014**, *26* (1), 10–28.
(25) Janssen, R. A. J.; Nelson, J. *Adv. Mater.* **2013**, *25* (13), 1847–1858.
(26) Ferguson, A. J.; Blackburn, J. L.; Kopidakis, N. *Mater. Lett.* **2013**, *90*, 115–125.
(27) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270* (5243), 1789–1791.
(28) Jang, S.-R.; Vittal, R.; Kim, K.-J. *Langmuir* **2004**, *20* (22), 9807–9810.
(29) Iwan, A.; Chuchmała, A. *Prog. Polym. Sci.* **2012**, *37* (12), 1805–1828.
(30) Maçaira, J.; Andrade, L.; Mendes, A. *Renew. Sustain. Energy Rev.* **2013**, *27*, 334–349.
(31) Habisreutinger, S. N.; Leijtens, T.; Eperon, G. E.; Stranks, S. D.; Nicholas, R. J.; Snaith, H. J. *Nano Lett.* **2014**, *14* (10), 5561–5568.
(32) Janani, M.; Srikrishnarka, P.; Nair, S. V.; Nair, A. S. *J Mater Chem A* **2015**.

(33) Bartelmess, J.; Ballesteros, B.; de la Torre, G.; Kiessling, D.; Campidelli, S.; Prato, M.; Torres, T.; Guldi, D. M. *J. Am. Chem. Soc.* **2010**, *132* (45), 16202–16211.
(34) Raïssi, M.; Vignau, L.; Cloutet, E.; Ratier, B. *Org. Electron.* **2015**, *21*, 86–91.
(35) Bailey, S.; Visontai, D.; Lambert, C. J.; Bryce, M. R.; Frampton, H.; Chappell, D. *J. Chem. Phys.* **2014**, *140* (5), 054708.
(36) Mann, J. A.; Rodríguez-López, J.; Abruña, H. D.; Dichtel, W. R. *J. Am. Chem. Soc.* **2011**, *133* (44), 17614–17617.
(37) Karachevtsev, V. A.; Stepanian, S. G.; Glamazda, A. Y.; Karachevtsev, M. V.; Eremenko, V. V.; Lytvyn, O. S.; Adamowicz, L. *J. Phys. Chem. C* **2011**, *115* (43), 21072–21082.
(38) Singh, M.; Holzinger, M.; Tabrizian, M.; Winters, S.; Berner, N. C.; Cosnier, S.; Duesberg, G. S. *J. Am. Chem. Soc.* **2015**, *137* (8), 2800–2803.
(39) D'Souza, F.; Chitta, R.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; D'Souza, L.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2007**, *129* (51), 15865–15871.
(40) Sibley, S. P.; Nguyen, Y. T.; Campbell, R. L.; Silber, H. B. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **1997**, *53* (5), 679–684.
(41) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118* (47), 11771–11782.
(42) Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100* (39), 15926–15932.
(43) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121* (40), 9378–9387.
(44) Araki, Y.; Chitta, R.; Sandanayaka, A. S. D.; Langenwalter, K.; Gadde, S.; Zandler, M. E.; Ito, O.; D'Souza, F. *J. Phys. Chem. C* **2008**, *112* (6), 2222–2229.
(45) D'Souza, F.; Deviprasad, G. R.; Zandler, M. E.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. B* **2002**, *106* (19), 4952–4962.
(46) Poddutoori, P. K.; Sandanayaka, A. S. D.; Hasobe, T.; Ito, O.; van der Est, A. *J. Phys. Chem. B* **2010**, *114* (45), 14348–14357.
(47) Nojiri, T.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1998**, *102* (27), 5215–5219.
(48) Rothemund, P. *J. Am. Chem. Soc.* **1936**, *58* (4), 625–627.
(49) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52* (5), 827–836.
(50) Adler, A. D.; Longo, F. R.; Shergalis, W. *J. Am. Chem. Soc.* **1964**, *86* (15), 3145–3149.
(51) Lindsey, J. S. *Acc. Chem. Res.* **2010**, *43* (2), 300–311.
(52) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64* (8), 2864–2872.
(53) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
(54) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393* (1–3), 51–57.
(55) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72* (10), 5639–5648.
(56) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105* (8), 2999–3094.
(57) Tenderholt, A. L. *QMForge*; Standford University: Standford, CA.
(58) Hua, Y.; Jiang, F.; Crivello, J. V. *Chem. Mater.* **2002**, *14* (5), 2369–2377.
(59) Saha, A.; Ramakrishnan, S. *Macromolecules* **2009**, *42* (14), 4956–4959.
(60) Kyatskaya, S.; Mascarós, J. R. G.; Bogani, L.; Hennrich, F.; Kappes, M.; Wernsdorfer, W.; Ruben, M. *J. Am. Chem. Soc.* **2009**, *131* (42), 15143–15151.
(61) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118* (18), 4354–4360.
(62) Zhang, C.; Long, H.; Zhang, W. *Chem. Commun.* **2012**, *48* (49), 6172–6174.

(63) Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Sabin, J. R.; Reina, G.; Galloni, P.; Floris, B. *Inorg. Chem.* **2010**, *49* (16), 7497–7509.
(64) Giasson, R.; Lee, E. J.; Zhao, X.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97* (11), 2596–2601.
(65) Solntsev, P. V.; Sabin, J. R.; Dammer, S. J.; Gerasimchuk, N. N.; Nemykin, V. N. *Chem. Commun.* **2010**, *46* (35), 6581–6583.
(66) Rochford, J.; Rooney, A. D.; Pryce, M. T. *Inorg. Chem.* **2007**, *46* (18), 7247–7249.
(67) Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99* (12), 3951–3958.
(68) Barker, C. A.; Zeng, X.; Bettington, S.; Batsanov, A. S.; Bryce, M. R.; Beeby, A. *Chem. – Eur. J.* **2007**, *13* (23), 6710–6717.
(69) Zaragoza-Galán, G.; Fowler, M. A.; Duhamel, J.; Rein, R.; Solladié, N.; Rivera, E. *Langmuir* **2012**, *28* (30), 11195–11205.
(70) Zaragoza-Galán, G.; Fowler, M.; Rein, R.; Solladié, N.; Duhamel, J.; Rivera, E. *J. Phys. Chem. C* **2014**, *118* (16), 8280–8294.
(71) Imahori, H.; Tamaki, K.; Yamada, H.; Yamada, K.; Sakata, Y.; Nishimura, Y.; Yamazaki, I.; Fujitsuka, M.; Ito, O. *Carbon* **2000**, *38* (11–12), 1599–1605.
(72) Sugunan, S. K.; Robotham, B.; Sloan, R. P.; Szmytkowski, J.; Ghiggino, K. P.; Paige, M. F.; Steer, R. P. *J. Phys. Chem. A* **2011**, *115* (44), 12217–12227.
(73) Mukherjee, P.; Bhattacharya (Banerjee), S.; Nayak, S. K.; Chattopadhyay, S.; Bhattacharya, S. *Chem. Phys.* **2009**, *360* (1–3), 116–122.

Appendix

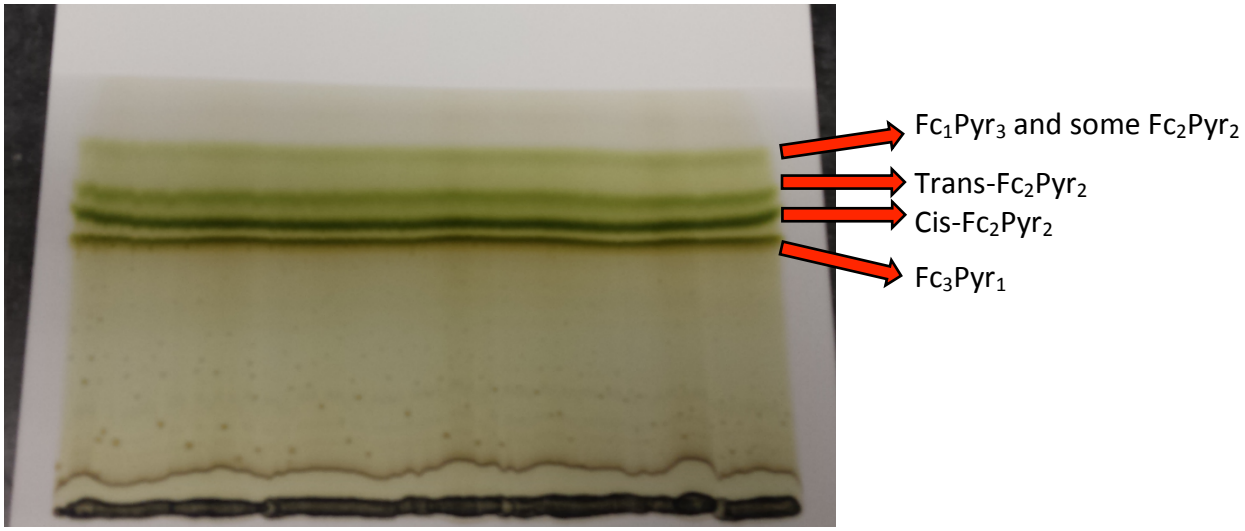

Figure A1. Separation of ferrocenyl porphyrins on 20x20 cm silica TLC with DCM/Toluene/EtOAc (12/8/1, v/v) as the eluent.

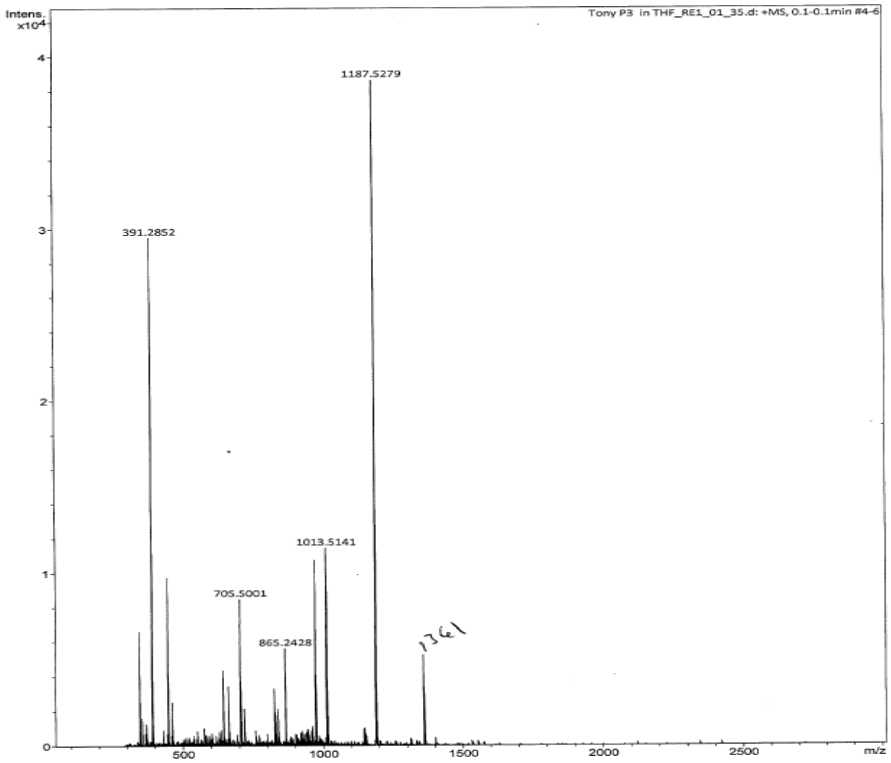

Figure A2. HRMS of reaction mixture of porphyrins 1a, 1b, and 5,10,15-tri[4-(1-pyrenylmethoxy)phenyl]-20-(4-*t*-butylphenyl) porphyrin (1013, 1187, and 1361 m/z, respectively).

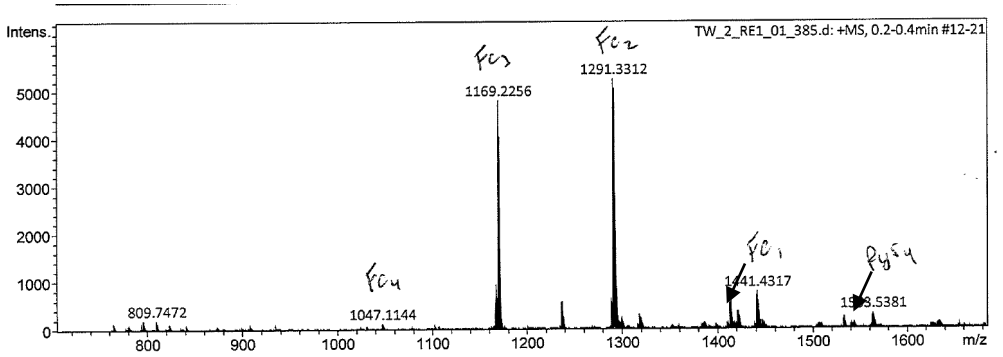

Figure A3. HRMS of reaction mixture of tetra ferrocenyl porphyrin, 2a, 2b, 5-ferrocenyl-10,15,20-tri[4-(1-pyrenylmethoxy)phenyl] porphyrin, and tetra-pyrenyl porphyrin (1047, 1169, 1291, 1413, and 1535 m/z, respectively)

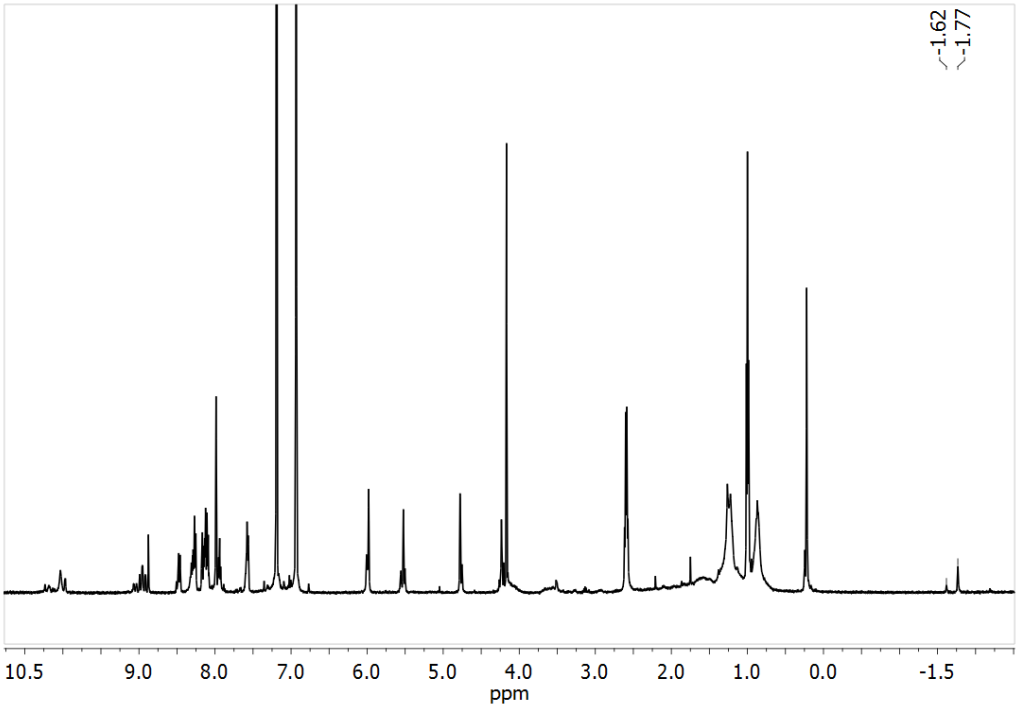

Figure A4. ^{1}H NMR of cis-2b in ODCB. The N-H shift at -1.77 ppm is indicative of a cis isomer, while the signal at -1.62 ppm is indicative of trans-2b.

Table A1. Geometry optimized coordinates of target porphyrins **1a**, **1b**, **2a**, and **2b**.

Porphyrin **1a** (*t*-butyl A1B3)

C	-7.36415900	-2.28564900	0.48582100
C	-6.46987400	-3.30043700	0.43200500
C	-5.16765600	-2.68755900	0.18562100

N	-5.27657100	-1.32784100	0.09603400
C	-6.60461300	-1.05716400	0.27094900
C	-6.04844600	3.66159500	0.04149600
C	-7.06893800	2.75867500	0.17631900
C	-6.50399800	1.44023900	0.17208700
N	-5.14565600	1.59957100	0.01906700
C	-4.81777700	2.93327200	-0.07034400
C	-7.19713900	0.22406600	0.29150400
C	-0.14751000	2.31780300	-0.67408500
C	-1.04238500	3.33227100	-0.61927100
C	-2.33847600	2.72160200	-0.34018100
N	-2.22618300	1.36342100	-0.23458900
C	-0.89999900	1.09169800	-0.42437200
C	-3.53110100	3.47077100	-0.23957900
C	-1.45198000	-3.62439900	-0.13035600
C	-0.43021100	-2.72176000	-0.25905400
C	-0.99638700	-1.40424700	-0.28625700
N	-2.35700900	-1.56366100	-0.15246000
C	-2.68475500	-2.89644300	-0.05041000
C	-3.97365700	-3.43500100	0.10189100
C	-0.30268500	-0.18859700	-0.42218900
C	1.18334900	-0.27872000	-0.57614500
C	-8.68414900	0.31436900	0.45836500
C	-9.24702900	0.83274800	1.63514000
C	-10.63174200	0.91661700	1.78770400
C	-11.47788700	0.48398700	0.76510200
C	-10.93044800	-0.03377700	-0.41024800
C	-9.54590900	-0.11788700	-0.56192100
C	1.76765800	-0.88187500	-1.70517900
C	3.14658600	-0.97204600	-1.84325600
C	3.99043100	-0.45709100	-0.84850900
C	3.43119700	0.15202300	0.28049700
C	2.04178800	0.23310900	0.40418600
O	5.32972400	-0.60017300	-1.07507400
C	6.23859900	-0.09117400	-0.10920100
H	-8.42661400	-2.34687500	0.67242000
H	-6.65601900	-4.35645900	0.56474400
H	-6.12614500	4.73812200	0.01681900
H	-8.12298700	2.97145300	0.27222500
H	-4.47696800	0.83694900	-0.02099100
H	0.91015000	2.37792400	-0.88580800
H	-0.86082100	4.38605400	-0.77430400
H	-1.37324700	-4.70029500	-0.08791500
H	0.62551500	-2.93546300	-0.32993200

H	-3.02672200	-0.80135300	-0.12582000
H	-8.59084800	1.16180500	2.43618700
H	-11.04861300	1.31569500	2.70875800
H	-11.58129900	-0.37000500	-1.21319000
H	-9.12189400	-0.51679100	-1.47920500
H	1.12660800	-1.27647600	-2.48843100
H	3.59430800	-1.43242700	-2.71860500
H	4.05616600	0.55806900	1.06724100
H	1.61761600	0.69985600	1.28863600
H	6.08510200	0.99296600	0.00375800
H	6.03321800	-0.55136100	0.86965500
C	7.66050600	-0.38555200	-0.53843000
C	8.73659700	0.06139900	0.26447900
C	7.92179700	-1.10036900	-1.70829900
C	10.07729900	-0.23039800	-0.13802900
C	9.22608100	-1.38533500	-2.10418100
H	7.08757000	-1.43611700	-2.31240400
C	10.32147800	-0.96445800	-1.33915900
H	9.40121100	-1.94407800	-3.02040400
C	11.18001100	0.20774000	0.65694600
C	12.51927500	-0.08720400	0.25357000
C	10.95169500	0.94210300	1.85972600
C	13.58537000	0.35430000	1.05286200
C	12.05031500	1.36371700	2.62697300
C	13.35161400	1.07154200	2.22549700
H	14.60397400	0.12969100	0.74574400
H	11.87326100	1.92297900	3.54248800
H	14.19079600	1.40468900	2.83009700
C	12.72777400	-0.82810200	-0.96042500
C	11.67869600	-1.24581700	-1.71956400
C	9.59710500	1.22152600	2.24005200
C	8.54436100	0.80291500	1.48330500
H	13.74897200	-1.04918400	-1.26137800
H	11.84980400	-1.80542100	-2.63607100
H	9.42263100	1.78070100	3.15625200
H	7.53610600	1.03644500	1.81101800
C	-3.43558000	4.96463200	-0.32303600
C	-2.83291400	5.69976400	0.70982600
C	-3.94487700	5.66013900	-1.43080300
C	-2.74253300	7.09028900	0.63766900
H	-2.43918800	5.17267100	1.57437000
C	-3.85388700	7.05088500	-1.50407700
H	-4.40525900	5.10200400	-2.24141400
C	-3.25298600	7.77041700	-0.46965100

H	-2.27578300	7.64227900	1.44936200
H	-4.24877200	7.57112300	-2.37285600
C	-4.06819100	-4.92918400	0.18743800
C	-3.59299900	-5.61896200	1.31362000
C	-4.63578000	-5.66936700	-0.86134100
C	-3.68300400	-7.00967500	1.38933000
H	-3.15977000	-5.05651700	2.13616300
C	-4.72561700	-7.05986500	-0.78651800
H	-5.00320300	-5.14642700	-1.73990600
C	-4.24914100	-7.73451600	0.33911200
H	-3.31459700	-7.52571300	2.27214000
H	-5.16537300	-7.61600900	-1.61034300
H	-12.55619700	0.54896000	0.88360300
H	-3.18217800	8.85336800	-0.52643200
H	-4.31933600	-8.81740200	0.39782000

Porphyrin **1b** (*t*-butyl A2B2)

C	-3.61945600	-2.23069700	0.76193200
C	-2.73582700	-3.25605900	0.73767300
C	-1.43743400	-2.67144800	0.41623800
N	-1.53775000	-1.31775900	0.25401000
C	-2.85800100	-1.02417600	0.45130800
C	-2.25878300	3.66780400	-0.04985000
C	-3.28795400	2.78455600	0.13939400
C	-2.73691000	1.46214700	0.20866900
N	-1.37783700	1.59839200	0.03888700
C	-1.03676700	2.92140400	-0.12754800
C	-3.44156700	0.26169000	0.40718600
C	3.61945600	2.23069700	-0.76193200
C	2.73582700	3.25605900	-0.73767300
C	1.43743400	2.67144800	-0.41623800
N	1.53775000	1.31775900	-0.25401000
C	2.85800100	1.02417600	-0.45130800
C	0.25360900	3.43614300	-0.33673400
C	2.25878300	-3.66780400	0.04985000
C	3.28795400	-2.78455600	-0.13939400
C	2.73691000	-1.46214700	-0.20866900
N	1.37783700	-1.59839200	-0.03888700
C	1.03676700	-2.92140400	0.12754800
C	-0.25360900	-3.43614300	0.33673400
C	3.44156700	-0.26169000	-0.40718600
C	4.92361200	-0.37517600	-0.58319900

C	-4.92361200	0.37517600	0.58319900
C	-5.48155400	1.02572100	1.69906700
C	-6.85689600	1.13668800	1.85721300
C	-7.72341300	0.59549400	0.89651400
C	-7.19049100	-0.06039600	-0.21898100
C	-5.80443600	-0.16190700	-0.36313400
C	5.48155400	-1.02572100	-1.69906700
C	6.85689600	-1.13668800	-1.85721300
C	7.72341300	-0.59549400	-0.89651400
C	7.19049100	0.06039600	0.21898100
C	5.80443600	0.16190700	0.36313400
O	-9.05724900	0.76119100	1.14026200
O	9.05724900	-0.76119100	-1.14026200
C	9.98640100	-0.23497600	-0.20344200
C	-9.98640100	0.23497600	0.20344200
H	-4.67472300	-2.27059800	0.98982200
H	-2.92606600	-4.30048400	0.93883300
H	-2.32568300	4.74190700	-0.13532300
H	-4.33919700	3.01445800	0.22501300
H	-0.71862200	0.82655900	0.03157400
H	4.67472300	2.27059800	-0.98982200
H	2.92606600	4.30048400	-0.93883300
H	2.32568300	-4.74190700	0.13532300
H	4.33919700	-3.01445800	-0.22501300
H	0.71862200	-0.82655900	-0.03157400
H	-4.82256400	1.44126000	2.45617500
H	-7.28423600	1.63392900	2.72254000
H	-7.83335800	-0.48753900	-0.97969000
H	-5.40076400	-0.66546900	-1.23692600
H	4.82256400	-1.44126000	-2.45617500
H	7.28423600	-1.63392900	-2.72254000
H	7.83335800	0.48753900	0.97969000
H	5.40076400	0.66546900	1.23692600
H	9.84479500	0.85329000	-0.11712700
H	9.79233700	-0.66680400	0.79046800
H	-9.79233700	0.66680400	-0.79046800
H	-9.84479500	-0.85329000	0.11712700
C	-11.39866300	0.55313500	0.64706600
C	-12.49034600	0.10895100	-0.13611000
C	-11.63619500	1.28408000	1.81198400
C	-13.82218800	0.42028200	0.28074500
C	-12.93187100	1.58815700	2.22180500
H	-10.79018700	1.61740100	2.40088500
C	-14.04205400	1.17071700	1.47642600

H	-13.08856200	2.15928500	3.13371900
C	-14.94018900	-0.01471000	-0.49437000
C	-12.32261000	-0.64900700	-1.34840400
C	-15.39090400	1.47130700	1.87162200
H	-11.32146100	-0.89793600	-1.68636400
C	-16.45460200	1.05654000	1.13141600
C	-16.27060500	0.29963000	-0.07665400
C	-14.73609900	-0.76533500	-1.69144000
C	-13.38990200	-1.06442900	-2.08629100
C	-17.35209700	-0.13907100	-0.85659600
C	-15.84945000	-1.18332600	-2.43919300
C	-17.14196200	-0.87209700	-2.02392700
H	-13.23384400	-1.63610100	-2.99809500
H	-15.69077000	-1.75491000	-3.35045400
H	-17.99277500	-1.20265800	-2.61350700
H	-18.36397400	0.10032200	-0.53859600
H	-17.46918400	1.29229600	1.44341000
H	-15.54361500	2.04314100	2.78382900
C	11.39866300	-0.55313500	-0.64706600
C	12.49034600	-0.10895100	0.13611000
C	11.63619500	-1.28408000	-1.81198400
C	13.82218800	-0.42028200	-0.28074500
C	12.93187100	-1.58815700	-2.22180500
H	10.79018700	-1.61740100	-2.40088500
C	14.04205400	-1.17071700	-1.47642600
H	13.08856200	-2.15928500	-3.13371900
C	14.94018900	0.01471000	0.49437000
C	16.27060500	-0.29963000	0.07665400
C	14.73609900	0.76533500	1.69144000
C	17.35209700	0.13907100	0.85659600
C	15.84945000	1.18332600	2.43919300
C	17.14196200	0.87209700	2.02392700
H	18.36397400	-0.10032200	0.53859600
H	15.69077000	1.75491000	3.35045400
H	17.99277500	1.20265800	2.61350700
C	16.45460200	-1.05654000	-1.13141600
C	15.39090400	-1.47130700	-1.87162200
C	13.38990200	1.06442900	2.08629100
C	12.32261000	0.64900700	1.34840400
H	17.46918400	-1.29229600	-1.44341000
H	15.54361500	-2.04314100	-2.78382900
H	13.23384400	1.63610100	2.99809500
H	11.32146100	0.89793600	1.68636400
C	0.36287200	4.92324700	-0.49526700

C	0.97453400	5.70382700	0.49803600
C	-0.14040100	5.56633400	-1.63688400
C	1.07981300	7.08782100	0.35446000
H	1.36417200	5.21745200	1.38795300
C	-0.03467300	6.95042300	-1.78156200
H	-0.60767500	4.97233900	-2.41754100
C	0.57540600	7.71562700	-0.78599400
H	1.55369300	7.67562700	1.13632900
H	-0.42516400	7.42962500	-2.67557500
C	-0.36287200	-4.92324700	0.49526700
C	0.14040100	-5.56633400	1.63688400
C	-0.97453400	-5.70382700	-0.49803600
C	0.03467300	-6.95042300	1.78156200
H	0.60767500	-4.97233900	2.41754100
C	-1.07981300	-7.08782100	-0.35446000
H	-1.36417200	-5.21745200	-1.38795300
C	-0.57540600	-7.71562700	0.78599400
H	0.42516400	-7.42962500	2.67557500
H	-1.55369300	-7.67562700	-1.13632900
H	0.65784800	8.79339600	-0.89843300
H	-0.65784800	-8.79339600	0.89843300

Porphyrin **2a** (Fc A1B3):

C	1.41179700	-2.18918100	-1.23418800
C	0.51156400	-3.17491700	-1.45282200
C	-0.79546300	-2.62959700	-1.09306500
N	-0.68043300	-1.32546600	-0.69320600
C	0.65317600	-1.03673500	-0.76298600
C	0.22542200	3.64692900	-0.00878900
C	1.21461400	2.70418500	-0.08701700
C	0.59895400	1.42403800	-0.27791300
N	-0.76078800	1.64149000	-0.25645900
C	-1.03906700	2.98210500	-0.10061900
C	1.26594100	0.20911900	-0.50666400
C	-5.65156500	2.31707200	0.63635100
C	-4.77523200	3.34587600	0.58085700
C	-3.51073500	2.78325800	0.11886000
N	-3.63155600	1.43903100	-0.10076900
C	-4.93652900	1.13294900	0.18375400
C	-2.32090100	3.55223300	0.01495300
C	-4.55081100	-3.38907600	-1.25280000
C	-5.53033300	-2.49122700	-0.92476500

C	-4.90478700	-1.28503300	-0.46810600
N	-3.54733500	-1.49174900	-0.59064700
C	-3.28186400	-2.77296300	-1.02841300
C	-2.00890400	-3.35358600	-1.20792900
C	2.76328000	0.26478500	-0.53454100
C	3.45163900	0.94482100	-1.55588800
C	4.83923800	0.98604200	-1.58723500
C	5.58633100	0.34412700	-0.58895900
C	4.92279400	-0.33887800	0.43639200
C	3.52544100	-0.37264600	0.45100800
O	6.94292200	0.44412200	-0.71112100
C	7.76321200	-0.18481600	0.26297600
H	2.47632800	-2.21314300	-1.41640800
H	0.70360000	-4.15631800	-1.85796300
H	0.34395000	4.71044100	0.10635100
H	2.27982300	2.86902200	-0.02990400
H	-1.47598200	0.92959900	-0.37116900
H	-6.67433400	2.33594700	0.96956900
H	-4.94870500	4.37096000	0.87120200
H	-4.68066000	-4.39344900	-1.61652500
H	-6.59484900	-2.63737700	-1.01451700
H	-2.82128300	-0.81941500	-0.36371700
H	2.88549700	1.43720100	-2.34150500
H	5.36842500	1.50400600	-2.38117900
H	5.47276900	-0.84163900	1.22348500
H	3.01865000	-0.90447400	1.25134200
H	7.52593500	0.21743900	1.25972800
H	7.54518800	-1.26368500	0.28773400
C	-2.46372100	5.03112000	0.12471900
C	-3.46908100	5.81035900	-0.54503900
C	-1.78902400	5.92864800	1.02430600
C	-3.43955400	7.14178700	-0.03755800
H	-4.14114800	5.43117100	-1.30297500
C	-2.39473000	7.21538300	0.93088800
H	-0.98802000	5.65558400	1.69809700
H	-4.07424500	7.95848200	-0.35600200
H	-2.10443700	8.09411000	1.49241100
C	-1.90813700	-4.79229500	-1.58895000
C	-2.54240600	-5.45977100	-2.69389200
C	-0.97933000	-5.73516800	-1.02756600
C	-1.98046000	-6.76274600	-2.82969100
H	-3.28634900	-5.02158700	-3.34570800
C	-1.00612500	-6.93175800	-1.80180700
H	-0.35512200	-5.54970000	-0.16406300

H	-2.25447600	-7.49532300	-3.57787800
H	-0.41886200	-7.82197500	-1.61767400
C	-1.45120400	8.04592300	-2.41019500
C	-0.37628900	8.17488000	-1.48061700
C	-1.41829700	6.72249600	-2.94319400
H	-2.17705200	8.81133900	-2.65279200
C	0.32240300	6.93094900	-1.44075000
H	-0.13793600	9.05771200	-0.90159800
C	-0.32308200	6.03318800	-2.34437300
H	-2.11216200	6.30838100	-3.66307300
H	1.19358500	6.71337400	-0.83635800
H	-0.04419100	5.00407600	-2.52603300
C	-4.17046000	-8.13263600	-0.81091700
C	-3.15833900	-8.23598200	0.18962200
C	-4.84637700	-6.88919700	-0.62615000
H	-4.38141100	-8.86398500	-1.58033800
C	-3.20642500	-7.05599600	0.99078400
H	-2.45991400	-9.05483900	0.30436900
C	-4.24905100	-6.22416000	0.48746800
H	-5.67204700	-6.52237700	-1.22228400
H	-2.55485600	-6.82473200	1.82341700
H	-4.52548300	-5.25073800	0.86899200
Fe	-1.64901100	6.66798000	-0.89988100
Fe	-2.83847400	-6.57622200	-0.97641400
C	9.22162700	0.05291800	-0.06878300
C	10.22487200	-0.46207800	0.78598800
C	9.58690800	0.77275100	-1.20749200
C	11.59991200	-0.23104000	0.46813400
C	10.92459900	0.99808000	-1.52125300
H	8.80768100	1.16064600	-1.85231100
C	11.95055900	0.50952900	-0.70233300
H	11.18109900	1.56256900	-2.41447100
C	12.63098100	-0.73694600	1.31705000
C	9.92521800	-1.21626600	1.97516100
C	13.33996700	0.72806800	-0.99818800
H	8.88935500	-1.40804000	2.23755900
C	14.32064900	0.24598400	-0.18763000
C	14.00459700	-0.50278500	0.99802800
C	12.29650800	-1.47912800	2.48988500
C	10.90979600	-1.69883900	2.78383400
C	14.99864200	-1.00953700	1.84966500
C	13.32587600	-1.96688100	3.31198900
C	14.66131500	-1.73282900	2.99302600
H	10.65438600	-2.26547200	3.67615500

H	13.06772100	-2.53187800	4.20439200
H	15.44607500	-2.11673300	3.63918200
H	16.04333800	-0.83088700	1.60676700
H	15.36746500	0.42005100	-0.42467000
H	13.59201900	1.29317200	-1.89235000
C	-7.01807100	-0.29738900	0.28413200
C	-8.10400500	0.52734200	-0.17576800
C	-7.62377500	-1.45235000	0.89461700
C	-9.33612600	-0.12925900	0.10732000
H	-7.99415900	1.46962700	-0.69488300
Fe	-8.31767100	0.20414800	1.85889000
C	-9.03976200	-1.36052300	0.76381100
H	-7.08211000	-2.26082400	1.36627100
H	-10.32289400	0.24855700	-0.12744200
C	-9.61560000	1.21607300	3.09113700
C	-9.23963400	-0.02843300	3.67926000
C	-8.42978000	1.98553200	2.89369500
C	-7.82206600	-0.02940100	3.84312500
C	-7.32153100	1.21420200	3.35799200
H	-9.76098200	-2.07876900	1.13165000
H	-10.62180500	1.51891600	2.83174100
H	-9.91037700	-0.83846500	3.93531300
H	-8.38274200	2.98096800	2.47138800
H	-7.22832900	-0.83822300	4.24859400
H	-6.28195800	1.51109300	3.32361900
C	-5.55962400	-0.12737800	0.01831100

Porphyrin **2b** (Fc A2B2):

C	-3.55148500	-2.08433800	1.19121700
C	-2.68812900	-3.11642900	1.33379800
C	-1.39957100	-2.65077600	0.82746000
N	-1.48434600	-1.34847800	0.41681600
C	-2.78946800	-0.98747200	0.60562000
C	-2.31725300	3.59505600	-0.65733800
C	-3.31021300	2.69390700	-0.38164600
C	-2.70077400	1.43115500	-0.08360700
N	-1.34374500	1.61386500	-0.23067200
C	-1.05898000	2.91893800	-0.57064200
C	-3.37497900	0.26485400	0.31925100
C	3.55148500	2.08433800	-1.19121700
C	2.68812900	3.11642900	-1.33379800
C	1.39957100	2.65077600	-0.82746000

N	1.48434600	1.34847800	-0.41681600
C	2.78946800	0.98747200	-0.60562000
C	0.22387700	3.44686000	-0.82011200
C	2.31725300	-3.59505600	0.65733800
C	3.31021300	-2.69390700	0.38164600
C	2.70077400	-1.43115500	0.08360700
N	1.34374500	-1.61386500	0.23067200
C	1.05898000	-2.91893800	0.57064200
C	-0.22387700	-3.44686000	0.82011200
C	3.37497900	-0.26485400	-0.31925100
C	4.86209200	-0.38095900	-0.46909200
C	-4.86209200	0.38095900	0.46909200
C	-5.43844700	1.16908500	1.48177800
C	-6.81662200	1.26800000	1.62296000
C	-7.66652900	0.57841900	0.74602900
C	-7.11474200	-0.21093400	-0.26935600
C	-5.72591300	-0.30226800	-0.39447400
C	5.43844700	-1.16908500	-1.48177800
C	6.81662200	-1.26800000	-1.62296000
C	7.66652900	-0.57841900	-0.74602900
C	7.11474200	0.21093400	0.26935600
C	5.72591300	0.30226800	0.39447400
O	-9.00460900	0.74155000	0.96696900
O	9.00460900	-0.74155000	-0.96696900
C	9.91909500	-0.07018400	-0.11222000
C	-9.91909500	0.07018400	0.11222000
H	-4.59027900	-2.04617200	1.48507100
H	-2.88680100	-4.07913600	1.77927500
H	-2.42821300	4.63842100	-0.89671100
H	-4.37410400	2.87598200	-0.37805200
H	-0.62381100	0.91101900	-0.08967400
H	4.59027900	2.04617200	-1.48507100
H	2.88680100	4.07913600	-1.77927500
H	2.42821300	-4.63842100	0.89671100
H	4.37410400	-2.87598200	0.37805200
H	0.62381100	-0.91101900	0.08967400
H	-4.79189700	1.70190200	2.17338300
H	-7.25885500	1.87016500	2.41068100
H	-7.74509900	-0.75287700	-0.96475800
H	-5.30678300	-0.91640200	-1.18650000
H	4.79189700	-1.70190200	-2.17338300
H	7.25885500	-1.87016500	-2.41068100
H	7.74509900	0.75287700	0.96475800
H	5.30678300	0.91640200	1.18650000

H	9.73686400	1.01466900	-0.15684700
H	9.74828700	-0.38516700	0.92851300
H	-9.74828700	0.38516700	-0.92851300
H	-9.73686400	-1.01466900	0.15684700
C	0.37409600	4.88912500	-1.15894100
C	1.42260000	5.74823500	-0.67874300
C	-0.34872900	5.64797300	-2.14487900
C	1.37252300	6.98391900	-1.38683100
H	2.13546200	5.48478200	0.09066800
C	0.27038500	6.92337100	-2.29010400
H	-1.19165800	5.28656200	-2.71832700
H	2.03459600	7.82775900	-1.24202400
H	-0.04887500	7.70889800	-2.96289500
C	-0.37409600	-4.88912500	1.15894100
C	0.34872900	-5.64797300	2.14487900
C	-1.42260000	-5.74823500	0.67874300
C	-0.27038500	-6.92337100	2.29010400
H	1.19165800	-5.28656200	2.71832700
C	-1.37252300	-6.98391900	1.38683100
H	-2.13546200	-5.48478200	-0.09066800
H	0.04887500	-7.70889800	2.96289500
H	-2.03459600	-7.82775900	1.24202400
C	-0.43920300	8.26258200	0.95386700
C	-1.55762600	8.30040600	0.06846800
C	-0.48383300	7.02904300	1.66995800
H	0.31974100	9.02806100	1.05150900
C	-2.29492500	7.09001400	0.23895200
H	-1.79958600	9.10170300	-0.61766100
C	-1.62971600	6.30439400	1.22867700
H	0.23477700	6.69351200	2.40625000
H	-3.20279900	6.82224000	-0.28619000
H	-1.92795300	5.32178800	1.56789200
C	1.55762600	-8.30040600	-0.06846800
C	0.43920300	-8.26258200	-0.95386700
C	2.29492500	-7.09001400	-0.23895200
H	1.79958600	-9.10170300	0.61766100
C	0.48383300	-7.02904300	-1.66995800
H	-0.31974100	-9.02806100	-1.05150900
C	1.62971600	-6.30439400	-1.22867700
H	3.20279900	-6.82224000	0.28619000
H	-0.23477700	-6.69351200	-2.40625000
H	1.92795300	-5.32178800	-1.56789200
Fe	-0.36408600	6.68158300	-0.35423700
Fe	0.36408600	-6.68158300	0.35423700

C	-11.33913800	0.38459200	0.53333500
C	-12.42000400	-0.15924900	-0.20043000
C	-11.59402300	1.20086000	1.63636700
C	-13.75900700	0.14088600	0.20168400
C	-12.89652000	1.49468200	2.03148000
H	-10.75618500	1.60948300	2.18829800
C	-13.99652600	0.97974700	1.33365400
H	-13.06666600	2.13378000	2.89456000
C	-14.86672300	-0.39421900	-0.52388600
C	-12.23471100	-1.01075600	-1.34639200
C	-15.35216200	1.26590800	1.71605400
H	-11.22804100	-1.25519900	-1.67112700
C	-16.40600900	0.75558000	1.02308600
C	-16.20427600	-0.09166500	-0.12052000
C	-14.64523500	-1.23443000	-1.65671200
C	-13.29222900	-1.52097800	-2.03742500
C	-17.27536500	-0.62950800	-0.85109800
C	-15.74867700	-1.74986800	-2.35680100
C	-17.04824800	-1.44880400	-1.95627500
H	-13.12284400	-2.16161300	-2.89965900
H	-15.57673000	-2.38951300	-3.21910500
H	-17.89122500	-1.85529700	-2.50845200
H	-18.29263700	-0.39893600	-0.54400000
H	-17.42594400	0.98141600	1.32480200
H	-15.51816300	1.90556000	2.57959200
C	11.33913800	-0.38459200	-0.53333500
C	12.42000400	0.15924900	0.20043000
C	11.59402300	-1.20086000	-1.63636700
C	13.75900700	-0.14088600	-0.20168400
C	12.89652000	-1.49468200	-2.03148000
H	10.75618500	-1.60948300	-2.18829800
C	13.99652600	-0.97974700	-1.33365400
H	13.06666600	-2.13378000	-2.89456000
C	14.86672300	0.39421900	0.52388600
C	16.20427600	0.09166500	0.12052000
C	14.64523500	1.23443000	1.65671200
C	17.27536500	0.62950800	0.85109800
C	15.74867700	1.74986800	2.35680100
C	17.04824800	1.44880400	1.95627500
H	18.29263700	0.39893600	0.54400000
H	15.57673000	2.38951300	3.21910500
H	17.89122500	1.85529700	2.50845200
C	16.40600900	-0.75558000	-1.02308600
C	15.35216200	-1.26590800	-1.71605400

C	13.29222900	1.52097800	2.03742500
C	12.23471100	1.01075600	1.34639200
H	17.42594400	-0.98141600	-1.32480200
H	15.51816300	-1.90556000	-2.57959200
H	13.12284400	2.16161300	2.89965900
H	11.22804100	1.25519900	1.67112700

Table A2. TDDFT Predicted energies and expansion coefficients for vertical excitation energies in target porphyrins **1a**, **1b**, **2a**, and **2b**.

Porphyrin **1a** (*t*-butyl A_1B_3):
Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 2.0766 eV 597.04 nm f=0.0333 <S**2>=0.000
220 -> 223 0.41986
221 -> 222 0.55053
221 -> 223 -0.10790
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2641.29482806
Copying the excited state density for this state as the 1-particle RhoCI density.
Excited State 2: Singlet-A 2.2725 eV 545.59 nm f=0.0617 <S**2>=0.000
220 -> 222 -0.42508
221 -> 222 0.10852
221 -> 223 0.54596
Excited State 3: Singlet-A 3.0267 eV 409.63 nm f=2.1890 <S**2>=0.000
220 -> 223 0.56242
221 -> 222 -0.42228
Excited State 4: Singlet-A 3.0546 eV 405.89 nm f=2.2683 <S**2>=0.000
220 -> 222 0.55877
221 -> 223 0.43683
Excited State 5: Singlet-A 3.7497 eV 330.65 nm f=0.7955 <S**2>=0.000
219 -> 224 0.69223
Excited State 6: Singlet-A 3.8124 eV 325.21 nm f=0.0002 <S**2>=0.000
215 -> 226 0.13268
216 -> 222 0.63849
216 -> 223 -0.12428
221 -> 226 0.12129
Excited State 7: Singlet-A 3.9739 eV 311.99 nm f=0.0001 <S**2>=0.000
217 -> 224 -0.40743
218 -> 224 0.25747
219 -> 225 0.44859
219 -> 226 0.23429
Excited State 8: Singlet-A 3.9930 eV 310.51 nm f=0.3519 <S**2>=0.000
209 -> 222 -0.15932

215 -> 222 0.55601
215 -> 223 -0.10619
216 -> 226 0.14174
217 -> 222 -0.13166
218 -> 222 -0.23305
Excited State 9: Singlet-A 4.1452 eV 299.10 nm f=0.0274 <S**2>=0.000
215 -> 222 0.23045
217 -> 222 0.20170
217 -> 223 0.19679
218 -> 222 0.38696
218 -> 223 0.36744
221 -> 226 -0.10739
Excited State 10: Singlet-A 4.2716 eV 290.25 nm f=0.0003 <S**2>=0.000
219 -> 222 0.59212
219 -> 223 0.37560
Excited State 11: Singlet-A 4.2969 eV 288.54 nm f=0.0036 <S**2>=0.000
216 -> 222 0.13958
216 -> 223 0.63954
218 -> 222 0.10668
220 -> 226 0.14297
Excited State 12: Singlet-A 4.3001 eV 288.33 nm f=0.0002 <S**2>=0.000
219 -> 222 -0.37580
219 -> 223 0.59570
Excited State 13: Singlet-A 4.3661 eV 283.97 nm f=0.0212 <S**2>=0.000
214 -> 223 0.15838
215 -> 222 -0.18663
215 -> 223 -0.31529
216 -> 223 0.10064
217 -> 222 -0.16008
217 -> 223 0.18527
218 -> 222 -0.31127
218 -> 223 0.34571
Excited State 14: Singlet-A 4.3978 eV 281.93 nm f=0.0540 <S**2>=0.000
205 -> 223 0.12785
215 -> 223 0.55454
217 -> 223 0.10833
218 -> 222 -0.16682
218 -> 223 0.22113
221 -> 226 -0.14163
Excited State 15: Singlet-A 4.5111 eV 274.84 nm f=0.0066 <S**2>=0.000
213 -> 222 0.12785
214 -> 222 0.10125
214 -> 223 -0.29433
217 -> 223 0.10448

218 -> 223 0.21790
221 -> 225 -0.23903
221 -> 226 0.44630
Excited State 16: Singlet-A 4.5837 eV 270.49 nm f=0.0024 <S**2>=0.000
201 -> 222 -0.36633
201 -> 226 -0.11924
202 -> 222 -0.23842
203 -> 222 0.46642
214 -> 222 -0.12531
Excited State 17: Singlet-A 4.5874 eV 270.27 nm f=0.0075 <S**2>=0.000
201 -> 222 0.49618
203 -> 222 0.42267
203 -> 226 -0.12793
Excited State 18: Singlet-A 4.6265 eV 267.99 nm f=0.0057 <S**2>=0.000
202 -> 222 -0.12702
213 -> 222 -0.11033
213 -> 223 -0.19040
214 -> 222 0.49155
214 -> 223 -0.10813
220 -> 226 0.18294
221 -> 226 -0.14035
Excited State 19: Singlet-A 4.6720 eV 265.38 nm f=0.0052 <S**2>=0.000
206 -> 222 -0.11200
206 -> 223 -0.34374
214 -> 223 0.39656
220 -> 226 0.16570
221 -> 225 -0.14732
221 -> 226 0.27700
Excited State 20: Singlet-A 4.7081 eV 263.34 nm f=0.0054 <S**2>=0.000
203 -> 223 0.10857
206 -> 223 0.25553
213 -> 223 0.30611
216 -> 223 -0.11679
220 -> 225 -0.22767
220 -> 226 0.42989
Excited State 21: Singlet-A 4.7348 eV 261.86 nm f=0.0104 <S**2>=0.000
201 -> 223 0.14138
205 -> 223 -0.10712
206 -> 223 0.38898
212 -> 223 -0.16393
213 -> 222 -0.30053
214 -> 223 0.27777
221 -> 226 0.12627
Excited State 22: Singlet-A 4.7492 eV 261.06 nm f=0.0161 <S**2>=0.000

201 -> 222 0.11596
201 -> 223 0.19384
202 -> 223 0.11189
206 -> 223 -0.18608
209 -> 222 -0.10337
209 -> 223 0.18836
211 -> 223 -0.23257
212 -> 222 0.10264
212 -> 223 -0.11818
213 -> 222 -0.21529
213 -> 223 0.31405
214 -> 223 -0.18954
221 -> 224 0.14187
Excited State 23: Singlet-A 4.7642 eV 260.24 nm f=0.0202 <S**2>=0.000
203 -> 223 0.12649
218 -> 224 0.12843
221 -> 224 0.64219
Excited State 24: Singlet-A 4.7693 eV 259.96 nm f=0.0034 <S**2>=0.000
202 -> 223 -0.16140
203 -> 222 0.12395
203 -> 223 0.62250
221 -> 224 -0.12641
Excited State 25: Singlet-A 4.7969 eV 258.47 nm f=0.0827 <S**2>=0.000
201 -> 223 0.50221
202 -> 223 0.14012
205 -> 223 0.35814
213 -> 222 0.15886
Excited State 26: Singlet-A 4.8113 eV 257.69 nm f=0.0618 <S**2>=0.000
201 -> 223 -0.24543
205 -> 223 0.42630
209 -> 223 0.13844
212 -> 223 0.14284
213 -> 222 -0.35878
Excited State 27: Singlet-A 4.8395 eV 256.19 nm f=0.0957 <S**2>=0.000
207 -> 224 0.12112
208 -> 224 -0.15738
217 -> 224 -0.15512
218 -> 224 0.10067
219 -> 225 -0.15821
219 -> 231 0.60481
Excited State 28: Singlet-A 4.8542 eV 255.42 nm f=0.0258 <S**2>=0.000
201 -> 223 0.13811
202 -> 223 0.16467
205 -> 223 -0.19325

209 -> 222 0.13254
209 -> 223 -0.12418
212 -> 222 -0.16178
212 -> 223 0.25764
213 -> 222 -0.22030
213 -> 223 -0.18049
214 -> 222 -0.24883
214 -> 223 -0.14602
220 -> 226 0.15583

Excited State 29: Singlet-A 4.8673 eV 254.73 nm f=0.7180 <S**2>=0.000
217 -> 224 0.40240
218 -> 224 -0.24502
219 -> 225 0.39549
219 -> 226 0.20372
219 -> 231 0.24091

Excited State 30: Singlet-A 4.9723 eV 249.35 nm f=0.0034 <S**2>=0.000
206 -> 222 -0.11194
209 -> 222 0.27309
209 -> 223 -0.21380
210 -> 222 0.26562
210 -> 223 0.34681
210 -> 226 0.11734
212 -> 222 0.27731
212 -> 223 -0.11440
215 -> 222 0.10364

Excited State 31: Singlet-A 4.9854 eV 248.69 nm f=0.0072 <S**2>=0.000
206 -> 222 -0.11183
209 -> 222 -0.19542
209 -> 223 0.19118
210 -> 223 0.10388
211 -> 222 -0.25517
211 -> 223 0.37752
212 -> 222 0.21743
213 -> 223 -0.12887

Excited State 32: Singlet-A 4.9990 eV 248.02 nm f=0.0042 <S**2>=0.000
205 -> 223 -0.12116
210 -> 222 0.23863
211 -> 223 0.20060
212 -> 222 -0.10008
212 -> 223 0.33617
213 -> 223 0.28982
214 -> 222 0.25371
220 -> 226 -0.13864

Excited State 33: Singlet-A 5.0490 eV 245.56 nm f=0.0117 <S**2>=0.000

205 -> 223 -0.10193
206 -> 222 0.11449
207 -> 222 0.25152
207 -> 223 0.18840
208 -> 222 0.20261
208 -> 223 0.14060
209 -> 222 -0.15687
209 -> 223 0.20814
210 -> 222 0.16959
211 -> 222 0.10667
213 -> 223 -0.19281
214 -> 222 -0.12234
218 -> 227 0.15753
221 -> 227 0.14394

Excited State 34: Singlet-A 5.0549 eV 245.27 nm f=0.0115 <S**2>=0.000
206 -> 223 0.16156
207 -> 222 -0.17758
208 -> 222 -0.13728
209 -> 223 0.20096
210 -> 222 0.31031
211 -> 222 0.13085
211 -> 223 -0.23169
212 -> 223 0.18167
213 -> 223 -0.12444
218 -> 227 -0.14957
221 -> 227 -0.13768

Excited State 35: Singlet-A 5.0716 eV 244.47 nm f=0.0003 <S**2>=0.000
207 -> 224 -0.38729
208 -> 224 0.51954
219 -> 231 0.19548

Excited State 36: Singlet-A 5.1026 eV 242.98 nm f=0.0017 <S**2>=0.000
220 -> 224 0.68830

Excited State 37: Singlet-A 5.1072 eV 242.76 nm f=0.0407 <S**2>=0.000
209 -> 222 0.21708
209 -> 223 0.33010
211 -> 222 -0.32306
212 -> 222 -0.29017
212 -> 223 -0.15109
213 -> 222 0.17369
214 -> 222 -0.10025
220 -> 224 -0.12688

Excited State 38: Singlet-A 5.1386 eV 241.28 nm f=0.0110 <S**2>=0.000
206 -> 222 0.54324
206 -> 223 -0.11827

210 -> 223 0.20365
211 -> 223 0.11316
212 -> 222 -0.12775
220 -> 226 0.13165
221 -> 227 -0.10213
Excited State 39: Singlet-A 5.1542 eV 240.55 nm f=0.1096 <S**2>=0.000
205 -> 222 0.57463
205 -> 223 -0.11593
209 -> 222 0.12815
209 -> 223 0.13167
210 -> 223 -0.19325
211 -> 223 0.13506
Excited State 40: Singlet-A 5.2249 eV 237.29 nm f=0.0002 <S**2>=0.000
200 -> 223 0.16923
202 -> 222 0.25214
206 -> 222 0.28964
209 -> 222 0.12716
210 -> 223 -0.26435
211 -> 222 -0.23328
212 -> 222 0.32161
Excited State 41: Singlet-A 5.2504 eV 236.14 nm f=0.0256 <S**2>=0.000
205 -> 222 0.10215
207 -> 222 -0.26488
207 -> 223 -0.18962
207 -> 235 -0.10375
208 -> 222 -0.21160
208 -> 223 -0.15454
217 -> 222 0.10089
217 -> 227 0.12645
218 -> 227 0.22878
218 -> 228 0.11355
221 -> 227 0.32243
221 -> 228 0.11505
Excited State 42: Singlet-A 5.2698 eV 235.27 nm f=0.0019 <S**2>=0.000
206 -> 223 -0.10396
209 -> 223 -0.14858
210 -> 222 0.41289
210 -> 223 -0.30602
211 -> 223 0.12208
212 -> 222 -0.13039
212 -> 223 -0.32281
213 -> 222 -0.13341
Excited State 43: Singlet-A 5.2912 eV 234.32 nm f=0.0119 <S**2>=0.000
205 -> 222 -0.21642

209 -> 222 0.36492
209 -> 223 0.19907
211 -> 222 0.37939
211 -> 223 0.25474
215 -> 222 0.10242
221 -> 228 -0.13046
Excited State 44: Singlet-A 5.3178 eV 233.15 nm f=0.0034 <S**2>=0.000
217 -> 222 0.49980
217 -> 223 0.33360
218 -> 222 -0.26452
218 -> 223 -0.18550
Excited State 45: Singlet-A 5.3308 eV 232.58 nm f=0.0370 <S**2>=0.000
200 -> 222 -0.11107
202 -> 223 0.24636
221 -> 227 -0.23039
221 -> 228 0.43188
221 -> 229 -0.12077
221 -> 230 -0.15428
Excited State 46: Singlet-A 5.3390 eV 232.22 nm f=0.0005 <S**2>=0.000
207 -> 223 -0.11143
217 -> 222 -0.34295
217 -> 223 0.48223
218 -> 222 0.17628
218 -> 223 -0.25527
Excited State 47: Singlet-A 5.3584 eV 231.38 nm f=0.0299 <S**2>=0.000
200 -> 222 0.19753
201 -> 223 0.10451
202 -> 222 0.10268
202 -> 223 -0.27718
207 -> 222 -0.15107
207 -> 223 0.11322
208 -> 222 -0.12352
210 -> 222 -0.10215
210 -> 223 0.12792
221 -> 228 0.32214
221 -> 229 -0.14494
221 -> 230 -0.10273
221 -> 232 -0.11022
Excited State 48: Singlet-A 5.3652 eV 231.09 nm f=0.0268 <S**2>=0.000
202 -> 222 -0.11394
221 -> 227 -0.15148
221 -> 228 0.21623
221 -> 229 0.42927
221 -> 230 0.38488

Excited State 49: Singlet-A 5.3797 eV 230.47 nm f=0.0206 <S**2>=0.000
200 -> 222 -0.13205
200 -> 223 0.14179
202 -> 222 0.25487
202 -> 223 0.12651
207 -> 223 0.16909
208 -> 223 0.12359
210 -> 223 0.10602
212 -> 222 -0.11781
217 -> 223 0.15575
221 -> 227 -0.11146
221 -> 229 -0.16808
221 -> 230 0.35844
Excited State 50: Singlet-A 5.3936 eV 229.87 nm f=0.0446 <S**2>=0.000
200 -> 223 0.10025
202 -> 222 0.13605
202 -> 223 0.10464
207 -> 223 0.15848
208 -> 223 0.11841
212 -> 222 -0.10896
221 -> 229 0.42278
221 -> 230 -0.31572
Excited State 51: Singlet-A 5.4465 eV 227.64 nm f=0.0192 <S**2>=0.000
200 -> 223 0.16403
202 -> 222 0.33654
203 -> 222 0.11274
207 -> 222 0.20962
207 -> 223 -0.27867
208 -> 222 0.15713
208 -> 223 -0.22136
212 -> 222 -0.10971
221 -> 235 -0.13195
Excited State 52: Singlet-A 5.4683 eV 226.73 nm f=0.1796 <S**2>=0.000
210 -> 229 -0.10134
211 -> 230 -0.10756
212 -> 229 0.10590
213 -> 233 -0.13914
214 -> 232 -0.16547
217 -> 225 -0.14511
218 -> 225 0.11621
221 -> 234 0.41762
221 -> 235 -0.10642
Excited State 53: Singlet-A 5.4710 eV 226.62 nm f=0.0260 <S**2>=0.000
209 -> 233 -0.10005

210 -> 223 -0.13228
210 -> 228 0.13933
210 -> 230 -0.10176
212 -> 229 0.12808
213 -> 228 -0.11308
213 -> 232 -0.11945
213 -> 234 -0.13633
214 -> 233 -0.13601
221 -> 232 0.21569
221 -> 233 0.43251
Excited State 54: Singlet-A 5.4827 eV 226.14 nm f=0.0584 <S**2>=0.000
200 -> 222 0.13348
202 -> 223 -0.21876
210 -> 230 0.10402
211 -> 230 0.12682
214 -> 232 0.11755
214 -> 234 -0.16440
221 -> 232 0.37349
221 -> 233 -0.21318
Excited State 55: Singlet-A 5.4867 eV 225.97 nm f=1.0627 <S**2>=0.000
217 -> 225 0.40458
217 -> 226 0.21969
218 -> 224 -0.11415
218 -> 225 -0.28891
218 -> 226 -0.13873
219 -> 224 -0.10365
221 -> 232 0.12545
221 -> 234 0.15560
221 -> 235 0.11274
Excited State 56: Singlet-A 5.5311 eV 224.16 nm f=0.0806 <S**2>=0.000
204 -> 224 0.14298
217 -> 224 0.27223
218 -> 224 0.40348
218 -> 235 0.14248
221 -> 224 -0.10532
221 -> 235 0.34235
Excited State 57: Singlet-A 5.5613 eV 222.94 nm f=0.1910 <S**2>=0.000
204 -> 224 -0.10879
217 -> 224 -0.18469
217 -> 225 -0.22885
217 -> 226 -0.10545
218 -> 224 -0.29032
218 -> 235 0.10160
221 -> 227 -0.16269

221 -> 235 0.39653
Excited State 58: Singlet-A 5.6537 eV 219.30 nm f=0.0012 <S**2>=0.000
204 -> 224 0.28130
207 -> 225 -0.18218
208 -> 225 0.23999
208 -> 226 0.12482
217 -> 231 0.32573
218 -> 224 -0.14453
218 -> 231 -0.19137
219 -> 236 -0.29735
Excited State 59: Singlet-A 5.7246 eV 216.58 nm f=0.0190 <S**2>=0.000
200 -> 223 -0.24892
202 -> 222 0.10461
218 -> 227 -0.17990
220 -> 227 -0.20080
220 -> 228 0.30051
220 -> 229 -0.13620
221 -> 225 -0.13591
221 -> 227 0.24113
221 -> 228 0.14542
221 -> 233 0.12907
221 -> 235 0.12620
Excited State 60: Singlet-A 5.7286 eV 216.43 nm f=0.0042 <S**2>=0.000
200 -> 223 0.20436
218 -> 227 0.13477
220 -> 227 -0.20884
220 -> 228 0.37853
221 -> 227 -0.16972
221 -> 230 -0.14570
221 -> 233 0.22830
Excited State 61: Singlet-A 5.7393 eV 216.03 nm f=0.0007 <S**2>=0.000
220 -> 227 -0.14182
220 -> 229 0.42906
220 -> 230 0.21339
221 -> 232 -0.34411
Excited State 62: Singlet-A 5.7565 eV 215.38 nm f=0.0043 <S**2>=0.000
200 -> 223 0.44884
202 -> 222 -0.20084
218 -> 227 -0.12941
220 -> 230 0.21006
221 -> 225 -0.12749
221 -> 227 0.19771
Excited State 63: Singlet-A 5.7712 eV 214.83 nm f=0.0194 <S**2>=0.000
220 -> 229 -0.24481

220 -> 230 0.39215
220 -> 233 0.11158
221 -> 225 0.10540
221 -> 233 -0.13166
221 -> 234 0.35279
Excited State 64: Singlet-A 5.8003 eV 213.75 nm f=0.0034 <S**2>=0.000
200 -> 222 0.37105
202 -> 223 0.20390
221 -> 225 0.41003
221 -> 226 0.18241
221 -> 227 0.10479
Excited State 65: Singlet-A 5.8116 eV 213.34 nm f=0.0046 <S**2>=0.000
200 -> 222 -0.35312
202 -> 223 -0.18852
220 -> 227 -0.16491
221 -> 225 0.36976
221 -> 226 0.23162
221 -> 235 0.15856
Excited State 66: Singlet-A 5.8582 eV 211.64 nm f=0.0059 <S**2>=0.000
204 -> 224 0.39697
218 -> 224 -0.10983
219 -> 236 0.43770
Excited State 67: Singlet-A 5.8632 eV 211.46 nm f=0.0039 <S**2>=0.000
204 -> 224 0.13518
210 -> 230 0.12628
211 -> 230 0.14304
214 -> 232 0.10772
214 -> 234 -0.10311
219 -> 236 0.14915
220 -> 227 0.26118
220 -> 228 -0.18451
220 -> 229 -0.13222
221 -> 232 -0.15383
221 -> 233 0.24126
221 -> 234 0.13018
221 -> 235 0.13312
Excited State 68: Singlet-A 5.8734 eV 211.10 nm f=0.0105 <S**2>=0.000
200 -> 222 -0.13665
220 -> 227 0.47680
220 -> 228 0.36728
220 -> 229 0.12808
Excited State 69: Singlet-A 5.8757 eV 211.01 nm f=0.0013 <S**2>=0.000
200 -> 223 -0.13956
209 -> 229 -0.15244

212 -> 229 -0.15684
213 -> 232 0.11112
220 -> 228 -0.16130
220 -> 229 0.36283
221 -> 232 0.24187
221 -> 233 0.14612
221 -> 234 0.15538
Excited State 70: Singlet-A 5.8851 eV 210.68 nm f=0.0045 <S**2>=0.000
200 -> 223 -0.12980
210 -> 228 -0.14054
210 -> 230 0.11715
211 -> 230 -0.10603
213 -> 233 -0.13100
220 -> 230 0.41242
221 -> 233 0.18918
221 -> 234 -0.22097
Excited State 71: Singlet-A 5.9817 eV 207.27 nm f=0.0018 <S**2>=0.000
220 -> 232 0.65181
220 -> 235 0.10486
Excited State 72: Singlet-A 5.9936 eV 206.86 nm f=0.0165 <S**2>=0.000
220 -> 230 -0.11731
220 -> 232 0.14047
220 -> 233 0.51889
220 -> 234 0.34704
220 -> 235 -0.14033
Excited State 73: Singlet-A 6.0040 eV 206.50 nm f=0.0140 <S**2>=0.000
204 -> 224 0.13769
217 -> 231 -0.11099
219 -> 236 -0.11639
220 -> 233 -0.38230
220 -> 234 0.45366
220 -> 235 -0.12690
Excited State 74: Singlet-A 6.0048 eV 206.47 nm f=0.0066 <S**2>=0.000
199 -> 224 0.14000
204 -> 224 0.30932
204 -> 225 -0.17147
207 -> 225 0.12189
208 -> 225 -0.13517
217 -> 231 -0.23873
217 -> 236 0.14623
218 -> 231 0.15549
219 -> 236 -0.24773
220 -> 233 0.13626
220 -> 234 -0.23831

Excited State 75: Singlet-A 6.0420 eV 205.20 nm f=0.0084 <S**2>=0.000
220 -> 225 -0.25247
220 -> 226 -0.11316
220 -> 234 0.25411
220 -> 235 0.55179
Excited State 76: Singlet-A 6.0508 eV 204.91 nm f=0.0017 <S**2>=0.000
199 -> 224 -0.27484
204 -> 224 0.17607
204 -> 225 0.28943
204 -> 226 0.15006
208 -> 224 -0.10261
208 -> 225 -0.15019
217 -> 231 -0.11610
217 -> 236 -0.26556
218 -> 236 0.16080
219 -> 236 -0.20542
219 -> 238 0.18251
Excited State 77: Singlet-A 6.1345 eV 202.11 nm f=0.0973 <S**2>=0.000
207 -> 227 0.16365
208 -> 227 0.12185
217 -> 235 0.22115
218 -> 225 -0.12659
218 -> 226 0.12476
218 -> 235 0.42283
221 -> 235 -0.21022
Excited State 78: Singlet-A 6.1465 eV 201.72 nm f=0.0056 <S**2>=0.000
220 -> 225 0.54960
220 -> 226 0.30256
220 -> 235 0.28601
Excited State 79: Singlet-A 6.2016 eV 199.92 nm f=0.0001 <S**2>=0.000
207 -> 222 -0.36635
207 -> 223 -0.22356
208 -> 222 0.47533
208 -> 223 0.28587
Excited State 80: Singlet-A 6.2279 eV 199.08 nm f=0.0001 <S**2>=0.000
207 -> 222 0.22412
207 -> 223 -0.37154
208 -> 222 -0.28732
208 -> 223 0.47501

Porphyrin **1b** (*t*-butyl A_2B_2):
Excited State 1: Singlet-AU 2.0717 eV 598.45 nm f=0.0397 <S**2>=0.000
280 -> 282 -0.36658
280 -> 283 0.21382

281 -> 282 0.28151
281 -> 283 0.48772
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3369.99724267
Copying the excited state density for this state as the 1-particle RhoCI density.
Excited State 2: Singlet-AU 2.2658 eV 547.20 nm f=0.0761 <S**2>=0.000
280 -> 282 0.21296
280 -> 283 0.37002
281 -> 282 0.48475
281 -> 283 -0.28225
Excited State 3: Singlet-AU 3.0202 eV 410.51 nm f=2.3093 <S**2>=0.000
280 -> 282 0.54560
280 -> 283 -0.14851
281 -> 282 0.10847
281 -> 283 0.40525
Excited State 4: Singlet-AU 3.0486 eV 406.70 nm f=2.2642 <S**2>=0.000
280 -> 282 0.14726
280 -> 283 0.54401
281 -> 282 -0.41545
281 -> 283 0.11507
Excited State 5: Singlet-AG 3.7491 eV 330.70 nm f=0.0000 <S**2>=0.000
278 -> 284 0.48933
279 -> 285 0.48929
Excited State 6: Singlet-AU 3.7496 eV 330.66 nm f=1.5893 <S**2>=0.000
278 -> 285 0.48950
279 -> 284 0.48979
Excited State 7: Singlet-AG 3.8126 eV 325.20 nm f=0.0000 <S**2>=0.000
272 -> 288 -0.13744
273 -> 282 0.32385
273 -> 283 0.55919
281 -> 288 -0.12696
Excited State 8: Singlet-AG 3.9740 eV 311.99 nm f=0.0000 <S**2>=0.000
274 -> 284 -0.22007
275 -> 285 -0.31488
276 -> 284 0.26020
277 -> 285 0.13053
278 -> 286 0.32460
278 -> 288 -0.15094
279 -> 287 0.35803
Excited State 9: Singlet-AU 3.9740 eV 311.99 nm f=0.0002 <S**2>=0.000
274 -> 285 -0.22001
275 -> 284 -0.31474
276 -> 285 0.25995
277 -> 284 0.13058

278 -> 287 0.35774
279 -> 286 0.32448
279 -> 288 -0.15090
Excited State 10: Singlet-AU 3.9860 eV 311.05 nm f=0.3503 <S**2>=0.000
268 -> 283 -0.13482
272 -> 282 0.28935
272 -> 283 0.49390
273 -> 288 -0.14775
274 -> 283 -0.21335
276 -> 283 -0.19413
Excited State 11: Singlet-AG 4.0698 eV 304.64 nm f=0.0000 <S**2>=0.000
273 -> 282 0.10315
275 -> 283 0.19100
277 -> 282 -0.21016
277 -> 283 0.58473
281 -> 288 0.12370
Excited State 12: Singlet-AU 4.2444 eV 292.11 nm f=0.0258 <S**2>=0.000
272 -> 282 0.26505
274 -> 282 -0.20184
274 -> 283 0.37557
276 -> 282 -0.19179
276 -> 283 0.37489
277 -> 288 0.12070
278 -> 283 0.11473
Excited State 13: Singlet-AG 4.2777 eV 289.84 nm f=0.0000 <S**2>=0.000
273 -> 282 -0.10525
279 -> 282 -0.16026
279 -> 283 0.66453
Excited State 14: Singlet-AU 4.2795 eV 289.72 nm f=0.0007 <S**2>=0.000
278 -> 282 -0.16347
278 -> 283 0.67367
Excited State 15: Singlet-AG 4.2891 eV 289.06 nm f=0.0000 <S**2>=0.000
273 -> 282 0.41346
273 -> 283 -0.30112
275 -> 282 -0.10753
277 -> 282 -0.32267
277 -> 283 -0.16542
279 -> 282 -0.12500
279 -> 283 0.14292
280 -> 288 0.15317
Excited State 16: Singlet-AG 4.3040 eV 288.07 nm f=0.0000 <S**2>=0.000
273 -> 282 0.11229
279 -> 282 0.66796
279 -> 283 0.18224

Excited State 17: Singlet-AU 4.3043 eV 288.05 nm f=0.0002 <S**2>=0.000
278 -> 282 0.68400
278 -> 283 0.17129
Excited State 18: Singlet-AG 4.3273 eV 286.52 nm f=0.0000 <S**2>=0.000
271 -> 282 0.12057
273 -> 282 0.36964
273 -> 283 -0.15165
275 -> 282 0.14902
277 -> 282 0.47251
277 -> 283 0.15095
279 -> 282 -0.10489
Excited State 19: Singlet-AU 4.3993 eV 281.83 nm f=0.0209 <S**2>=0.000
262 -> 282 0.12587
272 -> 282 0.43471
272 -> 283 -0.39750
274 -> 282 -0.14227
274 -> 283 -0.15899
276 -> 282 -0.12821
276 -> 283 -0.17442
Excited State 20: Singlet-AU 4.4961 eV 275.76 nm f=0.0967 <S**2>=0.000
272 -> 282 0.30878
274 -> 282 0.40424
274 -> 283 0.10847
276 -> 282 0.41964
276 -> 283 0.10718
Excited State 21: Singlet-AG 4.5118 eV 274.80 nm f=0.0000 <S**2>=0.000
271 -> 282 -0.32415
277 -> 282 0.17053
281 -> 286 0.23526
281 -> 288 0.48862
Excited State 22: Singlet-AG 4.5853 eV 270.40 nm f=0.0000 <S**2>=0.000
257 -> 288 0.15607
258 -> 282 0.29550
258 -> 283 0.49255
259 -> 282 0.18281
259 -> 283 0.29290
Excited State 23: Singlet-AU 4.5894 eV 270.15 nm f=0.0116 <S**2>=0.000
257 -> 282 0.35087
257 -> 283 0.56465
258 -> 288 0.13539
Excited State 24: Singlet-AG 4.6693 eV 265.53 nm f=0.0000 <S**2>=0.000
270 -> 288 -0.10501
271 -> 282 0.49649
271 -> 283 0.15685

277 -> 283 -0.10384
281 -> 286 0.14770
281 -> 288 0.31037
Excited State 25: Singlet-AG 4.6843 eV 264.68 nm f=0.0000 <S**2>=0.000
263 -> 282 -0.25413
263 -> 283 0.26973
271 -> 283 -0.29569
280 -> 286 0.19140
280 -> 288 0.40364
Excited State 26: Singlet-AG 4.7191 eV 262.73 nm f=0.0000 <S**2>=0.000
258 -> 283 -0.10076
262 -> 288 -0.10631
263 -> 282 0.46049
263 -> 283 -0.17973
271 -> 282 0.18845
280 -> 286 0.13700
280 -> 288 0.28923
281 -> 284 0.13922
Excited State 27: Singlet-AU 4.7429 eV 261.41 nm f=0.0456 <S**2>=0.000
277 -> 284 0.10538
281 -> 285 0.67865
Excited State 28: Singlet-AG 4.7468 eV 261.20 nm f=0.0000 <S**2>=0.000
281 -> 284 0.65964
Excited State 29: Singlet-AU 4.7684 eV 260.01 nm f=0.0070 <S**2>=0.000
257 -> 282 -0.37216
257 -> 283 0.30271
262 -> 282 0.14426
270 -> 282 0.43408
Excited State 30: Singlet-AG 4.7698 eV 259.94 nm f=0.0000 <S**2>=0.000
258 -> 282 0.48879
258 -> 283 -0.28683
259 -> 282 0.30082
259 -> 283 -0.18480
263 -> 282 -0.10020
Excited State 31: Singlet-AU 4.7986 eV 258.38 nm f=0.1351 <S**2>=0.000
257 -> 282 0.33778
257 -> 283 -0.17261
262 -> 282 0.44343
262 -> 283 -0.24202
263 -> 288 -0.10181
270 -> 282 0.16653
272 -> 282 -0.12410
Excited State 32: Singlet-AG 4.8391 eV 256.21 nm f=0.0000 <S**2>=0.000
265 -> 285 -0.11493

266 -> 284 -0.12085
275 -> 285 -0.12413
276 -> 284 0.10682
278 -> 286 -0.11826
278 -> 294 0.42656
279 -> 287 -0.13347
279 -> 293 0.42416
Excited State 33: Singlet-AU 4.8391 eV 256.21 nm f=0.2074 <S**2>=0.000
265 -> 284 -0.11496
266 -> 285 -0.12085
275 -> 284 -0.12404
276 -> 285 0.10666
278 -> 287 -0.13329
278 -> 293 0.42409
279 -> 286 -0.11813
279 -> 294 0.42670
Excited State 34: Singlet-AU 4.8493 eV 255.67 nm f=0.0591 <S**2>=0.000
257 -> 282 0.29835
257 -> 283 -0.10540
262 -> 282 -0.27059
262 -> 283 0.17106
268 -> 282 -0.24343
270 -> 282 0.38194
270 -> 283 0.16525
Excited State 35: Singlet-AG 4.8567 eV 255.28 nm f=0.0000 <S**2>=0.000
258 -> 282 -0.10757
269 -> 282 -0.29153
271 -> 282 -0.13258
271 -> 283 0.48492
277 -> 282 0.10971
280 -> 286 0.10448
280 -> 288 0.21902
Excited State 36: Singlet-AU 4.8670 eV 254.75 nm f=1.4307 <S**2>=0.000
274 -> 285 0.21624
275 -> 284 0.30850
276 -> 285 -0.25218
277 -> 284 -0.12319
278 -> 287 0.31375
278 -> 293 0.17414
279 -> 286 0.28565
279 -> 288 -0.12998
279 -> 294 0.17549
Excited State 37: Singlet-AG 4.8670 eV 254.74 nm f=0.0000 <S**2>=0.000
274 -> 284 0.21644

275 -> 285 0.30848
276 -> 284 -0.25231
277 -> 285 -0.12327
278 -> 286 0.28563
278 -> 288 -0.13016
278 -> 294 0.17542
279 -> 287 0.31396
279 -> 293 0.17414
Excited State 38: Singlet-AU 4.9868 eV 248.62 nm f=0.0091 <S**2>=0.000
262 -> 283 0.15864
264 -> 283 0.10168
268 -> 282 0.52030
268 -> 283 0.21466
269 -> 288 -0.13181
270 -> 282 0.22506
272 -> 282 0.10370
Excited State 39: Singlet-AG 4.9951 eV 248.21 nm f=0.0000 <S**2>=0.000
263 -> 283 0.17501
265 -> 283 -0.10871
267 -> 283 0.14269
268 -> 288 -0.11152
269 -> 282 0.51565
269 -> 283 0.21752
271 -> 283 0.20683
Excited State 40: Singlet-AU 5.0546 eV 245.29 nm f=0.0160 <S**2>=0.000
262 -> 282 0.15305
264 -> 282 -0.10069
264 -> 283 0.38968
266 -> 283 0.23379
268 -> 282 -0.12384
274 -> 290 0.12308
276 -> 290 0.11744
277 -> 289 0.21596
281 -> 290 0.21047
281 -> 292 0.10397
Excited State 41: Singlet-AG 5.0568 eV 245.18 nm f=0.0000 <S**2>=0.000
263 -> 282 0.18762
265 -> 283 -0.24361
267 -> 283 0.35740
269 -> 282 -0.20774
271 -> 283 -0.12144
274 -> 289 0.12970
276 -> 289 0.12433
277 -> 290 0.17621

281 -> 289 0.22783
Excited State 42: Singlet-AU 5.0714 eV 244.48 nm f=0.0006 <S**2>=0.000
264 -> 285 -0.22483
265 -> 284 0.37243
266 -> 285 0.39916
267 -> 284 0.26711
278 -> 293 0.13793
279 -> 294 0.13857
Excited State 43: Singlet-AG 5.0714 eV 244.48 nm f=0.0000 <S**2>=0.000
264 -> 284 -0.22492
265 -> 285 0.37236
266 -> 284 0.39919
267 -> 285 0.26705
278 -> 294 0.13853
279 -> 293 0.13797
Excited State 44: Singlet-AU 5.0995 eV 243.13 nm f=0.0022 <S**2>=0.000
270 -> 283 -0.12834
280 -> 285 0.68525
Excited State 45: Singlet-AG 5.0997 eV 243.12 nm f=0.0000 <S**2>=0.000
280 -> 284 0.69789
Excited State 46: Singlet-AU 5.1051 eV 242.86 nm f=0.0412 <S**2>=0.000
268 -> 282 0.21667
268 -> 283 -0.11263
270 -> 282 -0.10148
270 -> 283 0.59986
272 -> 283 -0.10228
280 -> 285 0.14003
Excited State 47: Singlet-AG 5.1378 eV 241.32 nm f=0.0000 <S**2>=0.000
263 -> 282 0.29240
263 -> 283 0.48364
267 -> 282 0.11268
269 -> 282 -0.11567
269 -> 283 0.17155
277 -> 290 -0.10256
280 -> 288 -0.15766
281 -> 289 -0.14707
Excited State 48: Singlet-AU 5.1533 eV 240.59 nm f=0.1272 <S**2>=0.000
262 -> 282 0.30682
262 -> 283 0.49833
264 -> 282 0.10819
268 -> 282 -0.15021
268 -> 283 0.16329
277 -> 289 -0.10423
281 -> 290 -0.13319

Excited State 49: Singlet-AG 5.2183 eV 237.60 nm f=0.0000 <S**2>=0.000
256 -> 282 0.15233
256 -> 283 -0.10847
258 -> 282 0.10439
258 -> 283 0.13200
259 -> 282 -0.15256
259 -> 283 -0.22241
263 -> 283 -0.21788
267 -> 282 0.13669
269 -> 282 -0.11132
269 -> 283 0.48855
Excited State 50: Singlet-AG 5.2383 eV 236.69 nm f=0.0000 <S**2>=0.000
259 -> 282 0.12234
263 -> 283 -0.18325
265 -> 283 -0.21759
267 -> 282 -0.12472
267 -> 283 0.32638
274 -> 289 -0.12607
276 -> 289 -0.11951
277 -> 290 -0.17755
281 -> 289 -0.31817
Excited State 51: Singlet-AU 5.2594 eV 235.74 nm f=0.0567 <S**2>=0.000
262 -> 283 -0.14970
264 -> 282 -0.10776
264 -> 283 0.35407
266 -> 283 0.21572
268 -> 283 -0.10043
274 -> 283 -0.10816
274 -> 290 -0.10873
276 -> 290 -0.10250
277 -> 289 -0.21122
281 -> 290 -0.34178
Excited State 52: Singlet-AU 5.2958 eV 234.12 nm f=0.0124 <S**2>=0.000
262 -> 283 -0.21639
268 -> 282 -0.12486
268 -> 283 0.57774
270 -> 283 0.19005
272 -> 283 0.12433
281 -> 292 -0.15776
Excited State 53: Singlet-AG 5.3064 eV 233.65 nm f=0.0000 <S**2>=0.000
256 -> 283 0.18015
258 -> 282 -0.21102
259 -> 282 0.34414
265 -> 282 0.15812

265 -> 283 0.10950
267 -> 282 -0.23950
267 -> 283 -0.17724
269 -> 283 0.27248
271 -> 283 -0.12700
275 -> 283 0.12045
281 -> 289 0.10113
Excited State 54: Singlet-AG 5.3237 eV 232.89 nm f=0.0000 <S**2>=0.000
269 -> 283 -0.14127
275 -> 282 -0.23337
275 -> 283 0.58350
277 -> 283 -0.19939
Excited State 55: Singlet-AU 5.3263 eV 232.78 nm f=0.0092 <S**2>=0.000
264 -> 283 -0.10281
274 -> 282 0.11985
274 -> 283 -0.46303
276 -> 282 -0.11745
276 -> 283 0.47680
Excited State 56: Singlet-AG 5.3399 eV 232.18 nm f=0.0000 <S**2>=0.000
267 -> 282 -0.15173
275 -> 282 0.53061
275 -> 283 0.27493
277 -> 282 -0.19355
Excited State 57: Singlet-AU 5.3451 eV 231.96 nm f=0.0002 <S**2>=0.000
264 -> 282 -0.12184
274 -> 282 0.47520
274 -> 283 0.12415
276 -> 282 -0.46239
276 -> 283 -0.11847
Excited State 58: Singlet-AG 5.3520 eV 231.66 nm f=0.0000 <S**2>=0.000
259 -> 283 -0.11274
281 -> 291 0.63496
Excited State 59: Singlet-AU 5.3565 eV 231.46 nm f=0.1127 <S**2>=0.000
268 -> 283 0.15563
281 -> 290 -0.29718
281 -> 292 0.56126
Excited State 60: Singlet-AG 5.3758 eV 230.63 nm f=0.0000 <S**2>=0.000
256 -> 282 0.21109
256 -> 283 0.13051
258 -> 283 0.16354
259 -> 282 0.14239
259 -> 283 -0.27415
265 -> 282 -0.13828
267 -> 282 0.17988

269 -> 283 -0.20398
275 -> 282 0.31783
281 -> 289 0.12390
281 -> 291 -0.12492
281 -> 295 -0.12058
Excited State 61: Singlet-AU 5.4205 eV 228.73 nm f=0.0099 <S**2>=0.000
262 -> 282 -0.11840
264 -> 282 0.51506
264 -> 283 0.16078
266 -> 282 0.30629
274 -> 282 0.10726
276 -> 282 -0.11576
281 -> 298 0.12146
Excited State 62: Singlet-AG 5.4548 eV 227.30 nm f=0.0000 <S**2>=0.000
256 -> 282 -0.15963
258 -> 283 -0.16870
259 -> 282 0.13557
259 -> 283 0.30107
265 -> 282 -0.24078
267 -> 282 0.35216
267 -> 283 0.10563
269 -> 283 0.14885
281 -> 295 -0.12092
281 -> 297 -0.15367
Excited State 63: Singlet-AU 5.4566 eV 227.22 nm f=0.3322 <S**2>=0.000
264 -> 282 -0.10730
268 -> 282 -0.10300
268 -> 292 -0.14316
269 -> 291 -0.18148
270 -> 283 0.10369
270 -> 296 0.16098
271 -> 295 -0.20448
281 -> 296 0.45199
281 -> 298 0.11431
Excited State 64: Singlet-AG 5.4718 eV 226.59 nm f=0.0000 <S**2>=0.000
259 -> 282 0.15895
268 -> 291 0.15505
269 -> 282 0.13372
269 -> 292 0.14774
270 -> 295 0.14906
271 -> 283 -0.10871
271 -> 296 -0.19238
275 -> 287 -0.10912
281 -> 295 0.43285

281 -> 297 -0.12369
Excited State 65: Singlet-AG 5.4824 eV 226.15 nm f=0.0000 <S**2>=0.000
256 -> 283 0.11083
274 -> 286 0.21459
274 -> 288 -0.11076
275 -> 287 0.35785
276 -> 286 -0.28945
276 -> 288 0.12592
277 -> 287 -0.17439
281 -> 295 0.13583
281 -> 297 0.18134
Excited State 66: Singlet-AU 5.4857 eV 226.01 nm f=2.3018 <S**2>=0.000
274 -> 287 0.25635
275 -> 286 0.34079
275 -> 288 -0.16530
276 -> 287 -0.33108
277 -> 284 -0.10759
277 -> 286 -0.16916
281 -> 296 0.13424
281 -> 298 -0.13318
Excited State 67: Singlet-AG 5.5192 eV 224.64 nm f=0.0000 <S**2>=0.000
256 -> 283 0.11294
274 -> 284 0.23531
275 -> 285 0.13388
276 -> 284 0.18342
277 -> 285 0.30190
277 -> 298 -0.13981
281 -> 297 0.38268
Excited State 68: Singlet-AU 5.5266 eV 224.34 nm f=0.2016 <S**2>=0.000
261 -> 284 0.10291
274 -> 285 0.26701
275 -> 284 0.15182
276 -> 285 0.20907
277 -> 284 0.34452
277 -> 297 0.12530
281 -> 285 -0.10306
281 -> 298 -0.32272
Excited State 69: Singlet-AG 5.5492 eV 223.43 nm f=0.0000 <S**2>=0.000
274 -> 284 -0.21090
274 -> 286 -0.14728
275 -> 285 -0.11510
275 -> 287 -0.21674
276 -> 284 -0.17297
276 -> 286 0.14435

277 -> 285 -0.27498
281 -> 289 -0.19397
281 -> 297 0.32415
Excited State 70: Singlet-AU 5.5588 eV 223.04 nm f=0.3865 <S**2>=0.000
274 -> 285 0.16450
274 -> 287 0.14468
275 -> 286 0.18215
276 -> 285 0.13709
276 -> 287 -0.14284
277 -> 284 0.21483
277 -> 297 -0.10711
281 -> 290 0.15898
281 -> 292 0.10147
281 -> 298 0.41507
Excited State 71: Singlet-AG 5.6524 eV 219.35 nm f=0.0000 <S**2>=0.000
260 -> 284 0.20530
261 -> 285 0.20227
264 -> 286 -0.10773
265 -> 287 0.19524
266 -> 286 0.18774
267 -> 287 0.13752
274 -> 294 0.17948
275 -> 293 0.24802
276 -> 294 -0.19801
277 -> 285 -0.10278
278 -> 299 -0.20736
279 -> 300 -0.20702
281 -> 289 -0.10097
Excited State 72: Singlet-AU 5.6532 eV 219.32 nm f=0.0031 <S**2>=0.000
260 -> 285 0.20325
261 -> 284 0.20000
264 -> 287 -0.12024
265 -> 286 0.17845
266 -> 287 0.20851
267 -> 286 0.12583
274 -> 293 0.17701
275 -> 294 0.25124
276 -> 293 -0.19970
277 -> 284 -0.11292
278 -> 300 -0.20993
279 -> 299 -0.21028
Excited State 73: Singlet-AU 5.6621 eV 218.97 nm f=0.0000 <S**2>=0.000
278 -> 285 0.50003
279 -> 284 -0.49979

Excited State 74: Singlet-AG 5.6621 eV 218.97 nm f=0.0000 <S**2>=0.000
278 -> 284 -0.49963
279 -> 285 0.50002
Excited State 75: Singlet-AG 5.7069 eV 217.25 nm f=0.0000 <S**2>=0.000
256 -> 282 0.27764
256 -> 283 -0.15241
259 -> 283 0.11325
274 -> 289 -0.17121
276 -> 289 -0.16349
277 -> 285 -0.10651
277 -> 290 -0.16023
277 -> 292 -0.10026
281 -> 286 -0.17851
281 -> 289 0.33627
281 -> 297 0.12630
Excited State 76: Singlet-AU 5.7238 eV 216.61 nm f=0.0268 <S**2>=0.000
274 -> 290 -0.14843
276 -> 290 -0.14254
277 -> 289 -0.19112
280 -> 290 -0.18179
280 -> 292 0.19120
281 -> 287 -0.25501
281 -> 290 0.32191
281 -> 292 0.21161
281 -> 298 -0.14019
Excited State 77: Singlet-AG 5.7312 eV 216.33 nm f=0.0000 <S**2>=0.000
268 -> 291 0.12358
269 -> 292 0.13809
270 -> 295 0.11337
280 -> 289 -0.10476
280 -> 291 0.47277
281 -> 295 -0.34664
Excited State 78: Singlet-AU 5.7449 eV 215.82 nm f=0.0113 <S**2>=0.000
269 -> 291 0.11501
280 -> 290 -0.31331
280 -> 292 0.37922
281 -> 287 0.13445
281 -> 290 -0.11537
281 -> 292 -0.11604
281 -> 296 0.33540
Excited State 79: Singlet-AG 5.7506 eV 215.60 nm f=0.0000 <S**2>=0.000
256 -> 282 0.40465
256 -> 283 -0.21794
258 -> 283 -0.10826

259 -> 282 0.11160
259 -> 283 0.17034
280 -> 291 -0.20385
281 -> 286 0.18487
281 -> 289 -0.21455
Excited State 80: Singlet-AG 5.7831 eV 214.39 nm f=0.0000 <S**2>=0.000
256 -> 283 0.25677
259 -> 282 -0.13528
281 -> 286 0.49865
281 -> 288 -0.21397
281 -> 289 0.14904
Excited State 81: Singlet-AU 5.7887 eV 214.18 nm f=0.0147 <S**2>=0.000
281 -> 287 0.61646
281 -> 290 0.15343
281 -> 298 -0.13780
Excited State 82: Singlet-AG 5.8019 eV 213.70 nm f=0.0000 <S**2>=0.000
256 -> 282 0.22552
256 -> 283 0.36026
258 -> 282 0.12004
259 -> 282 -0.17837
259 -> 283 0.13269
280 -> 289 0.23795
281 -> 286 -0.25580
281 -> 288 0.16337
281 -> 297 -0.19219
Excited State 83: Singlet-AU 5.8565 eV 211.70 nm f=0.0130 <S**2>=0.000
260 -> 285 0.28109
261 -> 284 0.27801
278 -> 300 0.30711
279 -> 299 0.30762
280 -> 290 -0.13447
281 -> 296 -0.13795
Excited State 84: Singlet-AG 5.8577 eV 211.66 nm f=0.0000 <S**2>=0.000
260 -> 284 0.29791
261 -> 285 0.29444
278 -> 299 0.32577
279 -> 300 0.32555
Excited State 85: Singlet-AU 5.8627 eV 211.48 nm f=0.0152 <S**2>=0.000
260 -> 285 0.10850
261 -> 284 0.10722
268 -> 292 0.16450
269 -> 291 0.18621
270 -> 296 -0.17666
271 -> 295 0.15703

278 -> 300 0.11859
279 -> 299 0.11901
280 -> 290 0.34075
280 -> 292 -0.15347
281 -> 296 0.27376
281 -> 298 -0.17395
Excited State 86: Singlet-AG 5.8675 eV 211.31 nm f=0.0000 <S**2>=0.000
256 -> 282 -0.17550
259 -> 283 -0.10687
268 -> 291 0.13968
269 -> 292 0.12154
270 -> 295 0.13138
271 -> 296 -0.11652
280 -> 289 0.44589
280 -> 291 -0.23932
281 -> 295 -0.23478
Excited State 87: Singlet-AG 5.8706 eV 211.20 nm f=0.0000 <S**2>=0.000
256 -> 283 -0.18639
268 -> 291 -0.12815
269 -> 292 -0.11456
270 -> 295 -0.11523
271 -> 296 0.10555
280 -> 289 0.42564
280 -> 291 0.32895
281 -> 295 0.18930
Excited State 88: Singlet-AU 5.8805 eV 210.84 nm f=0.0172 <S**2>=0.000
280 -> 290 0.43411
280 -> 292 0.49801
Excited State 89: Singlet-AG 5.9781 eV 207.40 nm f=0.0000 <S**2>=0.000
280 -> 295 0.66177
280 -> 297 0.10418
Excited State 90: Singlet-AU 5.9866 eV 207.10 nm f=0.0287 <S**2>=0.000
280 -> 287 0.13095
280 -> 293 0.10924
280 -> 296 0.63463
280 -> 298 0.17043
Excited State 91: Singlet-AG 6.0044 eV 206.49 nm f=0.0000 <S**2>=0.000
254 -> 285 0.10974
255 -> 284 0.10927
260 -> 284 0.23953
260 -> 286 -0.13702
261 -> 285 0.23752
261 -> 287 -0.15173
265 -> 287 -0.13723

266 -> 286 -0.11897
274 -> 294 -0.14224
275 -> 293 -0.20312
275 -> 300 0.12445
276 -> 294 0.17191
276 -> 299 -0.10067
278 -> 299 -0.19440
279 -> 300 -0.19405
Excited State 92: Singlet-AU 6.0044 eV 206.49 nm f=0.0019 <S**2>=0.000
254 -> 284 0.10970
255 -> 285 0.10921
260 -> 285 0.23939
260 -> 287 -0.15226
261 -> 284 0.23756
261 -> 286 -0.13631
265 -> 286 -0.12406
266 -> 287 -0.13104
274 -> 293 -0.14031
275 -> 294 -0.20523
275 -> 299 0.12448
276 -> 293 0.17076
276 -> 300 -0.10032
278 -> 300 -0.19437
279 -> 299 -0.19472
Excited State 93: Singlet-AG 6.0279 eV 205.68 nm f=0.0000 <S**2>=0.000
280 -> 286 -0.28352
280 -> 295 -0.12345
280 -> 297 0.58566
Excited State 94: Singlet-AU 6.0495 eV 204.95 nm f=0.0120 <S**2>=0.000
260 -> 287 0.10502
280 -> 287 0.28093
280 -> 296 -0.20248
280 -> 298 0.50280
Excited State 95: Singlet-AG 6.0506 eV 204.91 nm f=0.0000 <S**2>=0.000
254 -> 285 -0.19432
255 -> 284 -0.19458
260 -> 284 0.12495
260 -> 286 0.21046
261 -> 285 0.12345
261 -> 287 0.22995
266 -> 286 -0.11561
274 -> 299 -0.14484
275 -> 300 -0.20437
276 -> 299 0.16517

278 -> 299 -0.14587
278 -> 303 0.12920
279 -> 300 -0.14578
279 -> 302 0.12918
Excited State 96: Singlet-AU 6.0508 eV 204.91 nm f=0.0034 <S**2>=0.000
254 -> 284 0.17422
255 -> 285 0.17441
260 -> 285 -0.11559
260 -> 287 -0.20688
261 -> 284 -0.11414
261 -> 286 -0.18651
266 -> 287 0.11506
274 -> 300 0.13054
275 -> 299 0.18361
276 -> 300 -0.14662
278 -> 300 0.13150
278 -> 302 -0.11549
279 -> 299 0.13210
279 -> 303 -0.11549
280 -> 287 0.12487
280 -> 298 0.24842
Excited State 97: Singlet-AU 6.1221 eV 202.52 nm f=0.1895 <S**2>=0.000
264 -> 290 0.11682
267 -> 289 0.12120
274 -> 298 -0.24840
276 -> 298 -0.24688
277 -> 286 -0.13022
277 -> 288 -0.16888
277 -> 297 0.31260
281 -> 298 0.21463
Excited State 98: Singlet-AG 6.1377 eV 202.00 nm f=0.0000 <S**2>=0.000
264 -> 289 -0.15262
267 -> 290 -0.11941
274 -> 297 -0.24719
275 -> 298 0.10035
276 -> 297 -0.24521
277 -> 292 0.10179
277 -> 298 0.31214
280 -> 286 0.13374
281 -> 297 0.19416
Excited State 99: Singlet-AG 6.1435 eV 201.81 nm f=0.0000 <S**2>=0.000
280 -> 286 0.55127
280 -> 288 -0.27572
280 -> 289 0.10231

280 -> 297 0.27421
Excited State 100: Singlet-AU 6.1455 eV 201.75 nm f=0.0079 <S**2>=0.000
280 -> 287 0.61690
280 -> 298 -0.31321
Excited State 101: Singlet-AU 6.2079 eV 199.72 nm f=0.0006 <S**2>=0.000
264 -> 283 -0.34436
266 -> 282 -0.13718
266 -> 283 0.58775
Excited State 102: Singlet-AG 6.2086 eV 199.70 nm f=0.0000 <S**2>=0.000
265 -> 282 -0.13300
265 -> 283 0.56246
267 -> 283 0.38822
Excited State 103: Singlet-AU 6.2317 eV 198.96 nm f=0.0002 <S**2>=0.000
264 -> 282 -0.35054
266 -> 282 0.58931
266 -> 283 0.13999
Excited State 104: Singlet-AG 6.2321 eV 198.95 nm f=0.0000 <S**2>=0.000
265 -> 282 0.56638
265 -> 283 0.13293
267 -> 282 0.38726
Excited State 105: Singlet-AG 6.3034 eV 196.69 nm f=0.0000 <S**2>=0.000
280 -> 288 -0.11610
281 -> 301 0.66528
Excited State 106: Singlet-AU 6.3182 eV 196.23 nm f=0.0021 <S**2>=0.000
279 -> 286 0.29008
279 -> 288 0.59609
Excited State 107: Singlet-AG 6.3194 eV 196.19 nm f=0.0000 <S**2>=0.000
278 -> 286 0.29768
278 -> 288 0.61112
Excited State 108: Singlet-AU 6.3366 eV 195.66 nm f=0.0228 <S**2>=0.000
251 -> 282 -0.17834
251 -> 283 0.12453
253 -> 282 -0.10503
270 -> 292 0.10391
271 -> 291 0.11974
272 -> 283 0.10391
273 -> 286 0.18516
273 -> 288 0.38957
277 -> 288 -0.22654
279 -> 288 -0.13238
Excited State 109: Singlet-AU 6.3522 eV 195.18 nm f=0.0388 <S**2>=0.000
251 -> 283 -0.10093
268 -> 296 0.23645
269 -> 295 -0.24962

270 -> 290 -0.15112
270 -> 292 0.25804
271 -> 288 0.12137
271 -> 291 0.29825
277 -> 288 0.16636
280 -> 296 -0.11303
Excited State 110: Singlet-AG 6.3566 eV 195.05 nm f=0.0000 <S**2>=0.000
268 -> 291 -0.10721
268 -> 295 -0.26602
269 -> 296 0.28311
270 -> 291 0.29814
270 -> 295 -0.12726
271 -> 290 -0.17986
271 -> 292 0.26868
272 -> 291 -0.13154
280 -> 295 0.10610
Excited State 111: Singlet-AU 6.4281 eV 192.88 nm f=0.0991 <S**2>=0.000
251 -> 282 -0.16663
251 -> 283 -0.13625
269 -> 295 0.10626
273 -> 286 0.13121
273 -> 288 0.27583
277 -> 286 0.11930
277 -> 288 0.26032
278 -> 290 -0.20051
278 -> 292 -0.10939
279 -> 289 -0.23314
Excited State 112: Singlet-AG 6.4431 eV 192.43 nm f=0.0000 <S**2>=0.000
278 -> 289 0.46682
279 -> 290 0.40197
279 -> 292 0.21688
Excited State 113: Singlet-AU 6.4496 eV 192.24 nm f=0.0104 <S**2>=0.000
251 -> 282 -0.11065
277 -> 288 0.17913
278 -> 290 0.35048
278 -> 292 0.18757
279 -> 289 0.40652
Excited State 114: Singlet-AG 6.4924 eV 190.97 nm f=0.0000 <S**2>=0.000
261 -> 283 -0.12508
272 -> 286 -0.11121
272 -> 288 -0.22898
274 -> 284 -0.20288
274 -> 288 0.24033
276 -> 284 -0.27705

276 -> 288 0.23340
277 -> 285 0.30191
Excited State 115: Singlet-AU 6.4998 eV 190.75 nm f=0.0061 <S**2>=0.000
274 -> 285 -0.29407
276 -> 285 -0.40735
277 -> 284 0.44923
Excited State 116: Singlet-AG 6.5046 eV 190.61 nm f=0.0000 <S**2>=0.000
261 -> 283 0.10800
272 -> 286 0.10375
272 -> 288 0.21804
274 -> 284 -0.21802
274 -> 286 -0.10880
274 -> 288 -0.19507
276 -> 284 -0.30468
276 -> 286 -0.10291
276 -> 288 -0.19191
277 -> 285 0.33834
Excited State 117: Singlet-AU 6.5245 eV 190.03 nm f=0.0047 <S**2>=0.000
264 -> 287 -0.17278
265 -> 286 0.25689
265 -> 288 -0.11786
266 -> 287 0.29670
267 -> 286 0.17703
274 -> 293 -0.19346
275 -> 294 -0.27239
276 -> 293 0.21741
277 -> 294 0.10663
Excited State 118: Singlet-AG 6.5245 eV 190.03 nm f=0.0000 <S**2>=0.000
264 -> 286 -0.15891
265 -> 287 0.28403
266 -> 286 0.26933
266 -> 288 -0.12728
267 -> 287 0.19659
274 -> 294 -0.19402
275 -> 293 -0.27124
276 -> 294 0.21992
277 -> 287 -0.11635
277 -> 293 0.10875
Excited State 119: Singlet-AU 6.5336 eV 189.77 nm f=0.1096 <S**2>=0.000
247 -> 283 -0.15716
251 -> 282 0.26291
251 -> 283 0.29197
253 -> 282 0.15296
253 -> 283 0.18010

260 -> 282 0.11600
273 -> 288 0.17980
277 -> 288 0.25953
281 -> 293 -0.11588
Excited State 120: Singlet-AG 6.5405 eV 189.56 nm f=0.0000 <S**2>=0.000
274 -> 286 0.11544
277 -> 287 0.17592
281 -> 294 0.62227

Porphyrin **2a** (Fc A_1B_3):
Excited State 1: Singlet-A 1.9695 eV 629.54 nm f=0.1034 <S**2>=0.000
301 -> 303 -0.32433
301 -> 304 -0.19242
302 -> 303 -0.33428
302 -> 304 0.46615
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -6896.49852087
Copying the excited state density for this state as the 1-particle RhoCI density.
Excited State 2: Singlet-A 2.0874 eV 593.95 nm f=0.1342 <S**2>=0.000
295 -> 314 0.11171
298 -> 311 -0.18712
299 -> 313 -0.10656
301 -> 303 -0.16091
301 -> 304 0.20337
302 -> 303 0.38496
302 -> 304 0.27238
Excited State 3: Singlet-A 2.1522 eV 576.08 nm f=0.0044 <S**2>=0.000
294 -> 311 0.10579
294 -> 312 0.13998
294 -> 314 0.13680
295 -> 304 0.14102
295 -> 306 -0.12003
295 -> 311 0.37559
295 -> 313 0.11929
295 -> 316 -0.15133
296 -> 316 0.14000
298 -> 314 0.21743
298 -> 316 0.15409
Excited State 4: Singlet-A 2.1609 eV 573.77 nm f=0.0002 <S**2>=0.000
294 -> 314 0.13667
294 -> 316 -0.14052
296 -> 311 -0.16136
296 -> 312 0.22815

296 -> 313 0.10412
296 -> 314 -0.15800
297 -> 313 -0.14580
297 -> 315 0.10458
298 -> 306 0.10249
298 -> 311 0.11224
298 -> 312 -0.14479
298 -> 313 -0.12260
298 -> 316 0.16261
299 -> 303 0.13646
299 -> 312 0.19876
299 -> 315 -0.21204
Excited State 5: Singlet-A 2.1658 eV 572.47 nm f=0.0034 <S**2>=0.000
294 -> 311 0.23218
295 -> 314 -0.20770
295 -> 316 -0.17730
296 -> 312 0.14394
296 -> 314 0.13720
296 -> 316 -0.12649
297 -> 315 0.10184
298 -> 311 0.19995
298 -> 312 0.18595
298 -> 313 0.10192
299 -> 311 0.13449
299 -> 313 -0.11741
299 -> 314 0.10251
301 -> 303 -0.11805
302 -> 304 0.10191
Excited State 6: Singlet-A 2.1685 eV 571.76 nm f=0.0008 <S**2>=0.000
294 -> 312 -0.10417
294 -> 315 -0.13953
294 -> 316 0.12957
296 -> 311 -0.18768
296 -> 312 0.16555
296 -> 315 -0.14530
296 -> 316 -0.12050
297 -> 312 -0.11728
297 -> 313 0.25089
298 -> 314 -0.11546
298 -> 315 0.16720
299 -> 312 -0.19370
299 -> 314 0.16364
299 -> 316 -0.16942
Excited State 7: Singlet-A 2.1726 eV 570.67 nm f=0.0002 <S**2>=0.000

294 -> 313 0.21538
297 -> 303 -0.13988
297 -> 306 -0.11600
297 -> 312 -0.20758
297 -> 313 0.20374
297 -> 315 0.22500
297 -> 316 -0.21221
298 -> 313 -0.10638
299 -> 312 0.16551
299 -> 313 -0.13164
299 -> 315 0.20950
Excited State 8: Singlet-A 2.2132 eV 560.21 nm f=0.0458 <S**2>=0.000
294 -> 303 0.10367
294 -> 312 0.13089
294 -> 315 -0.12051
295 -> 312 -0.10236
295 -> 314 -0.11627
296 -> 314 -0.11704
297 -> 315 -0.15869
297 -> 316 0.10923
298 -> 311 0.14897
298 -> 312 -0.12592
299 -> 313 0.19529
299 -> 316 -0.10262
301 -> 303 -0.11245
301 -> 304 0.22107
302 -> 303 0.31623
302 -> 304 0.15192
Excited State 9: Singlet-A 2.5405 eV 488.03 nm f=0.0138 <S**2>=0.000
284 -> 311 -0.15528
285 -> 311 -0.17800
286 -> 311 0.15560
287 -> 311 -0.16799
288 -> 311 -0.12413
290 -> 311 0.10303
294 -> 311 0.12453
294 -> 313 0.10342
295 -> 312 0.12422
295 -> 313 0.15094
295 -> 314 0.25983
295 -> 316 0.15910
298 -> 311 0.13910
Excited State 10: Singlet-A 2.5524 eV 485.75 nm f=0.0040 <S**2>=0.000
282 -> 312 0.13129

285 -> 311 -0.10460
285 -> 312 0.13366
286 -> 311 -0.10405
286 -> 312 0.16240
288 -> 311 -0.10594
288 -> 312 0.14036
296 -> 314 0.23614
296 -> 315 -0.20056
296 -> 316 -0.14777
299 -> 312 0.12903
Excited State 11: Singlet-A 2.5580 eV 484.69 nm f=0.0049 <S**2>=0.000
286 -> 312 -0.13345
286 -> 313 0.18418
286 -> 316 -0.10982
287 -> 312 -0.17059
287 -> 313 0.20264
287 -> 316 -0.10856
294 -> 313 -0.13064
294 -> 315 0.11222
297 -> 315 0.28826
297 -> 316 -0.17085
299 -> 313 0.15814
Excited State 12: Singlet-A 2.5841 eV 479.80 nm f=0.0023 <S**2>=0.000
284 -> 314 -0.12138
285 -> 314 -0.11611
286 -> 314 0.11260
287 -> 314 -0.13035
288 -> 314 -0.10692
290 -> 314 0.12985
294 -> 314 -0.15632
294 -> 316 -0.12073
295 -> 311 0.24140
296 -> 314 -0.11300
298 -> 313 -0.11689
298 -> 314 -0.19594
298 -> 316 -0.12375
Excited State 13: Singlet-A 2.5908 eV 478.55 nm f=0.0017 <S**2>=0.000
282 -> 314 0.11788
285 -> 314 0.10498
286 -> 314 0.10925
286 -> 315 -0.12100
288 -> 314 0.13407
288 -> 315 -0.11045
294 -> 314 -0.10613

294 -> 316 0.11585
296 -> 311 -0.13743
296 -> 312 0.20727
298 -> 314 0.17229
298 -> 315 -0.10304
299 -> 314 -0.16487
299 -> 315 0.17989
Excited State 14: Singlet-A 2.5947 eV 477.83 nm f=0.0032 <S**2>=0.000
286 -> 313 -0.12366
286 -> 315 0.15867
287 -> 313 -0.12318
287 -> 315 0.22490
287 -> 316 -0.10563
290 -> 315 0.10471
294 -> 315 0.17250
297 -> 312 -0.16779
297 -> 313 0.25037
298 -> 315 -0.13277
299 -> 315 -0.20338
299 -> 316 0.14845
Excited State 15: Singlet-A 2.9179 eV 424.91 nm f=2.0328 <S**2>=0.000
301 -> 303 0.56986
302 -> 304 0.40063
Excited State 16: Singlet-A 2.9602 eV 418.83 nm f=1.9331 <S**2>=0.000
301 -> 304 0.59893
302 -> 303 -0.35991
Excited State 17: Singlet-A 3.3623 eV 368.75 nm f=0.0025 <S**2>=0.000
284 -> 311 0.13504
285 -> 311 0.14962
286 -> 311 -0.13268
287 -> 311 0.15868
288 -> 311 0.13745
290 -> 311 -0.14579
294 -> 311 0.13698
295 -> 304 -0.10792
295 -> 312 0.10469
295 -> 313 0.13377
295 -> 314 0.23487
295 -> 316 0.14181
298 -> 304 0.14849
298 -> 311 0.14384
Excited State 18: Singlet-A 3.3807 eV 366.74 nm f=0.0007 <S**2>=0.000
282 -> 312 -0.10219
285 -> 312 -0.10128

286 -> 312 -0.16848
287 -> 313 0.10187
288 -> 312 -0.14111
291 -> 312 0.11621
296 -> 314 0.19213
296 -> 315 -0.17549
296 -> 316 -0.11465
298 -> 303 -0.11723
299 -> 303 0.21210
299 -> 312 0.14110
Excited State 19: Singlet-A 3.3862 eV 366.14 nm f=0.0032 <S**2>=0.000
286 -> 313 -0.16013
286 -> 316 0.11168
287 -> 303 0.11043
287 -> 312 0.17880
287 -> 313 -0.17943
294 -> 312 0.11408
294 -> 313 -0.11010
297 -> 303 -0.15053
297 -> 315 0.23939
297 -> 316 -0.13803
298 -> 303 -0.13770
299 -> 303 -0.10922
299 -> 313 0.15163
Excited State 20: Singlet-A 3.4650 eV 357.82 nm f=0.0028 <S**2>=0.000
282 -> 314 0.10680
285 -> 314 0.18291
286 -> 315 -0.21866
287 -> 313 0.16447
287 -> 316 0.16707
288 -> 314 0.15515
294 -> 316 -0.11088
295 -> 304 0.11338
295 -> 311 0.11669
296 -> 303 -0.16279
296 -> 312 -0.12240
297 -> 303 -0.13141
297 -> 313 0.12238
298 -> 314 -0.17225
299 -> 303 0.12048
299 -> 315 -0.16280
Excited State 21: Singlet-A 3.4678 eV 357.53 nm f=0.0015 <S**2>=0.000
284 -> 314 -0.13407
285 -> 313 -0.12148

285 -> 316 -0.12278
286 -> 314 0.16167
287 -> 314 -0.20942
294 -> 304 -0.10042
294 -> 314 0.12500
295 -> 304 -0.16660
295 -> 311 -0.13523
296 -> 303 -0.12178
298 -> 313 0.12451
298 -> 316 0.10877
Excited State 22: Singlet-A 3.4780 eV 356.48 nm f=0.0061 <S**2>=0.000
285 -> 315 -0.10521
286 -> 313 -0.15260
286 -> 314 0.14709
286 -> 316 -0.14838
287 -> 315 0.25734
288 -> 314 0.10649
294 -> 303 0.15985
294 -> 315 -0.12528
297 -> 303 0.14968
297 -> 313 -0.13906
298 -> 315 0.13206
299 -> 314 0.12918
299 -> 316 -0.13318
Excited State 23: Singlet-A 3.7199 eV 333.30 nm f=0.0371 <S**2>=0.000
288 -> 304 0.16970
289 -> 304 -0.10834
290 -> 304 0.16456
291 -> 303 -0.24501
291 -> 304 0.33382
298 -> 303 -0.10579
298 -> 304 0.11071
299 -> 303 0.24704
299 -> 304 -0.12480
302 -> 306 0.18636
Excited State 24: Singlet-A 3.7506 eV 330.57 nm f=0.8017 <S**2>=0.000
292 -> 307 0.11130
300 -> 305 0.68881
Excited State 25: Singlet-A 3.7910 eV 327.05 nm f=0.0057 <S**2>=0.000
288 -> 304 -0.11465
290 -> 303 0.13474
290 -> 304 -0.12802
291 -> 304 -0.21820
298 -> 304 -0.10587

298 -> 316 -0.10579
299 -> 303 0.49990
299 -> 312 -0.12678
Excited State 26: Singlet-A 3.8489 eV 322.13 nm f=0.0606 <S**2>=0.000
289 -> 303 0.13206
289 -> 304 -0.12518
294 -> 303 -0.12998
296 -> 303 -0.15487
297 -> 303 0.19384
298 -> 303 0.48869
298 -> 312 -0.11379
299 -> 313 0.10471
Excited State 27: Singlet-A 3.8777 eV 319.74 nm f=0.0174 <S**2>=0.000
294 -> 304 0.14592
296 -> 303 0.16378
296 -> 304 0.13558
297 -> 303 -0.13978
297 -> 304 -0.13662
298 -> 304 0.39751
298 -> 311 -0.13759
299 -> 304 0.23723
Excited State 28: Singlet-A 3.8942 eV 318.38 nm f=0.0003 <S**2>=0.000
296 -> 303 0.37472
296 -> 312 -0.11390
297 -> 303 0.44057
297 -> 312 -0.10496
297 -> 313 0.13662
297 -> 316 -0.10939
Excited State 29: Singlet-A 3.9163 eV 316.59 nm f=0.0030 <S**2>=0.000
294 -> 303 -0.31387
295 -> 303 0.21086
296 -> 303 0.31687
296 -> 312 -0.10067
297 -> 303 -0.27286
297 -> 313 -0.10300
298 -> 303 0.14669
Excited State 30: Singlet-A 3.9435 eV 314.40 nm f=0.1982 <S**2>=0.000
288 -> 303 -0.11100
288 -> 304 0.23436
289 -> 303 -0.23735
289 -> 304 0.40329
291 -> 306 -0.10296
293 -> 304 -0.10925
295 -> 304 -0.19830

298 -> 303 0.17821
Excited State 31: Singlet-A 3.9565 eV 313.37 nm f=0.0292 <S**2>=0.000
289 -> 303 -0.10972
289 -> 304 0.14518
294 -> 304 0.14708
295 -> 303 0.16353
295 -> 304 0.48234
295 -> 311 -0.19213
295 -> 314 0.10063
295 -> 316 0.14420
296 -> 304 -0.11279
Excited State 32: Singlet-A 3.9739 eV 312.00 nm f=0.0001 <S**2>=0.000
292 -> 305 -0.42168
293 -> 305 0.23317
300 -> 307 0.50552
Excited State 33: Singlet-A 4.0168 eV 308.66 nm f=0.0478 <S**2>=0.000
294 -> 303 0.40021
296 -> 303 0.16559
297 -> 303 -0.15413
298 -> 303 0.23608
299 -> 304 -0.38622
Excited State 34: Singlet-A 4.0417 eV 306.76 nm f=0.0145 <S**2>=0.000
289 -> 304 -0.11020
290 -> 304 0.10046
291 -> 303 -0.11552
294 -> 303 0.17752
295 -> 303 -0.13679
296 -> 303 0.17739
298 -> 303 0.12702
298 -> 304 -0.28491
299 -> 304 0.42911
302 -> 306 0.12415
Excited State 35: Singlet-A 4.0840 eV 303.59 nm f=0.0153 <S**2>=0.000
294 -> 303 0.18916
294 -> 304 0.11627
295 -> 303 0.53020
295 -> 304 -0.22475
296 -> 303 -0.10914
296 -> 304 0.10284
297 -> 304 -0.11153
298 -> 304 -0.20569
Excited State 36: Singlet-A 4.1000 eV 302.40 nm f=0.0688 <S**2>=0.000
293 -> 304 -0.19507
294 -> 303 -0.16144

294 -> 304 0.36588
295 -> 303 -0.25968
297 -> 304 -0.30609
298 -> 304 -0.25775
299 -> 304 -0.10266
Excited State 37: Singlet-A 4.1346 eV 299.87 nm f=0.0049 <S**2>=0.000
291 -> 303 0.10597
294 -> 304 0.19192
296 -> 304 0.45483
297 -> 304 0.43280
298 -> 304 -0.12225
302 -> 306 -0.10204
Excited State 38: Singlet-A 4.1409 eV 299.41 nm f=0.0099 <S**2>=0.000
292 -> 304 -0.10434
293 -> 303 -0.16488
293 -> 304 -0.22591
294 -> 304 0.18491
295 -> 304 -0.14966
296 -> 304 -0.32302
297 -> 304 0.37115
298 -> 304 0.13733
302 -> 306 0.15451
Excited State 39: Singlet-A 4.1807 eV 296.56 nm f=0.0211 <S**2>=0.000
288 -> 303 -0.10849
290 -> 303 -0.13626
291 -> 303 -0.12018
292 -> 304 0.10388
293 -> 303 0.17612
293 -> 304 0.23788
294 -> 303 0.12738
294 -> 304 0.38141
295 -> 304 -0.15674
296 -> 304 -0.24895
302 -> 306 -0.23146
Excited State 40: Singlet-A 4.2378 eV 292.57 nm f=0.0131 <S**2>=0.000
288 -> 303 0.13308
288 -> 304 0.15577
289 -> 303 0.11597
290 -> 304 0.14454
291 -> 303 0.38328
291 -> 304 0.17971
296 -> 304 -0.10527
299 -> 303 0.15076
302 -> 306 -0.33664

Excited State 41: Singlet-A 4.2517 eV 291.61 nm f=0.0001 <S**2>=0.000
300 -> 303 0.69431
Excited State 42: Singlet-A 4.2795 eV 289.72 nm f=0.0109 <S**2>=0.000
289 -> 303 0.35529
289 -> 304 0.13441
290 -> 303 -0.17800
291 -> 303 -0.22482
291 -> 304 -0.13945
292 -> 304 -0.10870
293 -> 304 -0.24652
301 -> 306 0.10315
302 -> 306 -0.26330
Excited State 43: Singlet-A 4.3123 eV 287.52 nm f=0.0251 <S**2>=0.000
288 -> 303 0.22622
288 -> 304 0.15054
289 -> 303 0.34532
289 -> 304 0.28685
290 -> 303 0.21260
292 -> 304 0.10307
293 -> 304 0.23732
302 -> 306 0.13301
Excited State 44: Singlet-A 4.3189 eV 287.08 nm f=0.0006 <S**2>=0.000
300 -> 304 0.69337
Excited State 45: Singlet-A 4.3550 eV 284.69 nm f=0.0143 <S**2>=0.000
289 -> 303 0.15044
291 -> 303 0.16076
292 -> 303 0.22732
293 -> 303 0.51767
293 -> 304 -0.19466
302 -> 306 0.14448
Excited State 46: Singlet-A 4.4687 eV 277.45 nm f=0.0221 <S**2>=0.000
268 -> 304 -0.10029
269 -> 304 0.14858
276 -> 303 0.13192
288 -> 303 0.14857
289 -> 303 -0.10304
290 -> 303 0.30005
290 -> 304 -0.19935
291 -> 303 -0.21944
291 -> 304 0.12691
293 -> 303 0.13072
293 -> 304 -0.16466
302 -> 306 -0.21220
Excited State 47: Singlet-A 4.5075 eV 275.06 nm f=0.0092 <S**2>=0.000

268 -> 304 0.16305
269 -> 304 -0.14993
272 -> 304 0.12271
276 -> 304 0.10522
290 -> 303 0.24098
290 -> 304 0.35939
291 -> 303 -0.10450
299 -> 304 -0.11343
301 -> 306 0.28067
302 -> 306 -0.19007
Excited State 48: Singlet-A 4.5508 eV 272.44 nm f=0.0129 <S**2>=0.000
268 -> 303 0.11590
268 -> 304 -0.22131
268 -> 306 0.12348
269 -> 303 -0.26016
269 -> 304 0.38557
272 -> 304 -0.15305
288 -> 303 -0.11849
290 -> 304 0.19799
301 -> 306 0.15533
Excited State 49: Singlet-A 4.5737 eV 271.08 nm f=0.0019 <S**2>=0.000
268 -> 303 -0.23936
268 -> 304 0.38004
269 -> 303 -0.24896
269 -> 304 0.13290
269 -> 306 0.12198
285 -> 303 0.10330
288 -> 303 -0.17137
301 -> 306 -0.29295
Excited State 50: Singlet-A 4.5836 eV 270.49 nm f=0.0257 <S**2>=0.000
268 -> 303 0.21238
268 -> 304 -0.20444
269 -> 304 -0.19821
285 -> 303 0.10189
288 -> 303 -0.18729
301 -> 306 -0.20805
302 -> 305 0.45191
Excited State 51: Singlet-A 4.5899 eV 270.13 nm f=0.0051 <S**2>=0.000
268 -> 303 -0.14016
269 -> 304 0.16287
285 -> 303 -0.10398
288 -> 303 0.18808
290 -> 303 -0.11366
301 -> 306 0.23142

302 -> 305 0.52015
Excited State 52: Singlet-A 4.6406 eV 267.17 nm f=0.0590 <S**2>=0.000
269 -> 303 -0.10560
272 -> 303 0.19440
275 -> 303 -0.12659
276 -> 303 0.29311
276 -> 304 0.12419
277 -> 303 0.12673
278 -> 303 -0.17523
281 -> 303 -0.12526
284 -> 303 0.14400
285 -> 303 -0.11557
287 -> 303 -0.14477
288 -> 303 0.20597
290 -> 303 -0.24092
Excited State 53: Singlet-A 4.6856 eV 264.61 nm f=0.0095 <S**2>=0.000
276 -> 303 0.10213
276 -> 304 0.14062
281 -> 303 0.11199
285 -> 304 -0.18544
287 -> 303 0.10680
288 -> 303 -0.15819
288 -> 304 0.32701
289 -> 304 -0.13616
290 -> 304 -0.18943
291 -> 303 0.15507
291 -> 304 -0.18563
301 -> 306 0.17853
Excited State 54: Singlet-A 4.7444 eV 261.33 nm f=0.0177 <S**2>=0.000
268 -> 303 -0.14264
269 -> 303 0.41884
269 -> 304 0.26250
271 -> 303 0.19074
275 -> 303 -0.19165
291 -> 304 -0.16326
301 -> 306 -0.10761
Excited State 55: Singlet-A 4.7582 eV 260.57 nm f=0.0899 <S**2>=0.000
268 -> 303 0.28253
268 -> 304 0.19052
271 -> 303 0.24398
274 -> 303 -0.17352
275 -> 303 -0.25472
275 -> 304 -0.10013
280 -> 303 -0.10011

287 -> 303 0.13960
290 -> 303 -0.10019
290 -> 304 -0.11078
291 -> 304 0.16289
301 -> 306 0.10995
Excited State 56: Singlet-A 4.7644 eV 260.23 nm f=0.0442 <S**2>=0.000
268 -> 303 0.40381
268 -> 304 0.30381
269 -> 303 0.24823
269 -> 304 0.23174
271 -> 303 -0.17570
275 -> 303 0.12507
Excited State 57: Singlet-A 4.7778 eV 259.50 nm f=0.0029 <S**2>=0.000
268 -> 303 -0.18076
269 -> 303 0.18621
275 -> 303 0.10110
276 -> 303 0.16066
278 -> 303 -0.15141
284 -> 303 0.10332
284 -> 304 0.12002
287 -> 303 0.21776
287 -> 304 -0.12451
288 -> 303 -0.13102
288 -> 304 -0.17715
289 -> 303 0.11970
291 -> 304 0.21698
301 -> 306 0.11536
Excited State 58: Singlet-A 4.8333 eV 256.52 nm f=0.0005 <S**2>=0.000
286 -> 303 0.45364
286 -> 304 -0.11001
287 -> 303 0.34487
288 -> 303 0.15316
291 -> 303 -0.12652
Excited State 59: Singlet-A 4.8391 eV 256.21 nm f=0.1261 <S**2>=0.000
279 -> 305 0.17392
292 -> 305 0.17522
293 -> 305 -0.11298
300 -> 307 0.20534
300 -> 309 0.59627
Excited State 60: Singlet-A 4.8506 eV 255.61 nm f=0.0130 <S**2>=0.000
273 -> 303 0.10110
281 -> 303 0.14580
283 -> 303 -0.11951
285 -> 303 0.40443

286 -> 303 0.20292
287 -> 303 -0.31297
290 -> 304 -0.11985
291 -> 304 0.11649
301 -> 306 0.10839
Excited State 61: Singlet-A 4.8655 eV 254.82 nm f=0.7172 <S**2>=0.000
292 -> 305 0.40360
293 -> 305 -0.23042
300 -> 307 0.43959
300 -> 309 -0.26736
Excited State 62: Singlet-A 4.8671 eV 254.74 nm f=0.0063 <S**2>=0.000
284 -> 304 -0.15573
284 -> 311 -0.10049
285 -> 304 0.36335
286 -> 303 -0.12243
286 -> 304 -0.24724
287 -> 304 0.27006
288 -> 304 0.10118
Excited State 63: Singlet-A 4.9269 eV 251.65 nm f=0.0102 <S**2>=0.000
274 -> 303 0.14086
281 -> 303 -0.13461
283 -> 303 0.50800
283 -> 304 -0.11776
283 -> 306 0.12343
287 -> 303 -0.10680
288 -> 303 -0.18305
290 -> 304 -0.10857
291 -> 304 0.12521
301 -> 306 0.13156
Excited State 64: Singlet-A 4.9521 eV 250.37 nm f=0.0022 <S**2>=0.000
273 -> 303 -0.14878
282 -> 303 0.55243
282 -> 306 -0.13133
284 -> 303 -0.11456
284 -> 304 0.18773
Excited State 65: Singlet-A 4.9645 eV 249.74 nm f=0.0039 <S**2>=0.000
276 -> 303 -0.10602
278 -> 303 0.11054
282 -> 303 -0.12944
282 -> 304 0.16326
283 -> 303 0.10271
284 -> 303 0.16834
284 -> 304 0.44304
284 -> 306 -0.11982

285 -> 304 0.11374
286 -> 303 -0.10518
287 -> 304 0.11663
Excited State 66: Singlet-A 4.9843 eV 248.75 nm f=0.0069 <S**2>=0.000
272 -> 303 0.11298
275 -> 303 0.13844
281 -> 303 0.36261
283 -> 303 0.24248
284 -> 304 -0.16488
285 -> 303 0.13626
286 -> 303 -0.21694
288 -> 303 0.13234
290 -> 303 -0.17049
290 -> 304 0.12146
Excited State 67: Singlet-A 5.0523 eV 245.40 nm f=0.0495 <S**2>=0.000
271 -> 304 -0.15149
275 -> 303 -0.15521
279 -> 304 0.14270
280 -> 304 0.26691
281 -> 304 -0.18217
287 -> 304 -0.24100
289 -> 304 -0.13000
290 -> 304 -0.10015
293 -> 308 -0.18689
301 -> 305 -0.23512
302 -> 308 0.18829
Excited State 68: Singlet-A 5.0630 eV 244.88 nm f=0.0168 <S**2>=0.000
281 -> 304 -0.10898
287 -> 304 -0.16565
301 -> 305 0.63415
Excited State 69: Singlet-A 5.0708 eV 244.50 nm f=0.0364 <S**2>=0.000
271 -> 304 0.10782
272 -> 304 -0.10096
276 -> 304 -0.14722
277 -> 304 -0.10483
279 -> 304 0.11766
279 -> 305 -0.17918
280 -> 304 0.24503
281 -> 304 0.14831
284 -> 303 0.12213
287 -> 304 0.26688
289 -> 304 0.11525
293 -> 308 -0.16615
301 -> 305 0.13662

302 -> 308 0.16882
Excited State 70: Singlet-A 5.0730 eV 244.40 nm f=0.0038 <S**2>=0.000
279 -> 305 0.54143
280 -> 305 -0.28243
300 -> 309 -0.18373
301 -> 305 0.13645
Excited State 71: Singlet-A 5.1094 eV 242.66 nm f=0.0106 <S**2>=0.000
269 -> 304 -0.10279
272 -> 304 -0.13969
276 -> 304 -0.20780
277 -> 303 0.10951
277 -> 304 -0.16348
278 -> 304 0.19419
281 -> 303 -0.15228
284 -> 303 0.19098
285 -> 303 0.21495
286 -> 303 -0.19005
287 -> 303 0.16149
287 -> 304 -0.17781
288 -> 303 0.11800
293 -> 308 0.12103
302 -> 308 -0.13359
Excited State 72: Singlet-A 5.1267 eV 241.84 nm f=0.0032 <S**2>=0.000
272 -> 304 0.12569
276 -> 304 0.20253
278 -> 304 -0.16053
281 -> 303 -0.22605
281 -> 304 0.10548
284 -> 303 -0.10008
285 -> 303 0.26213
285 -> 304 -0.22579
286 -> 303 -0.16280
287 -> 303 0.19742
287 -> 304 0.10608
288 -> 304 -0.15633
302 -> 308 0.11852
Excited State 73: Singlet-A 5.1517 eV 240.67 nm f=0.0485 <S**2>=0.000
271 -> 304 -0.29972
274 -> 304 0.21070
275 -> 303 -0.11996
275 -> 304 0.30232
280 -> 304 0.11226
281 -> 304 -0.10905
286 -> 304 0.12239

287 -> 304 0.28564
293 -> 308 0.11386
302 -> 308 -0.15396
Excited State 74: Singlet-A 5.1668 eV 239.96 nm f=0.0019 <S**2>=0.000
281 -> 303 -0.11163
285 -> 303 0.14066
285 -> 304 0.21588
286 -> 304 0.55660
288 -> 304 0.18949
291 -> 304 -0.10028
Excited State 75: Singlet-A 5.2523 eV 236.06 nm f=0.0267 <S**2>=0.000
278 -> 304 0.13459
279 -> 303 -0.12750
279 -> 304 -0.14063
280 -> 303 -0.26680
280 -> 304 -0.30098
281 -> 304 -0.12702
285 -> 304 -0.11776
292 -> 303 -0.15329
293 -> 308 -0.15666
302 -> 308 0.30955
Excited State 76: Singlet-A 5.2610 eV 235.67 nm f=0.0357 <S**2>=0.000
275 -> 304 0.29821
281 -> 303 0.12606
281 -> 304 0.33976
283 -> 303 -0.11334
283 -> 304 -0.32482
285 -> 304 0.14787
287 -> 304 -0.17070
Excited State 77: Singlet-A 5.2947 eV 234.17 nm f=0.0041 <S**2>=0.000
280 -> 304 -0.14072
292 -> 303 0.59757
293 -> 303 -0.26195
Excited State 78: Singlet-A 5.3061 eV 233.67 nm f=0.0053 <S**2>=0.000
272 -> 303 -0.18156
276 -> 304 0.12539
277 -> 304 0.10498
278 -> 303 0.14803
282 -> 303 0.16052
282 -> 304 -0.10845
284 -> 303 0.49538
284 -> 304 -0.24273
Excited State 79: Singlet-A 5.3104 eV 233.47 nm f=0.0040 <S**2>=0.000
272 -> 303 -0.11303

273 -> 303 -0.10781
273 -> 304 0.10777
274 -> 304 0.14456
277 -> 304 0.18168
278 -> 304 0.10188
281 -> 304 0.28810
282 -> 304 -0.18979
283 -> 303 0.11350
283 -> 304 0.29617
285 -> 304 0.12952
292 -> 303 0.14404

Excited State 80: Singlet-A 5.3362 eV 232.34 nm f=0.0101 <S**2>=0.000
271 -> 303 -0.10020
273 -> 303 0.19201
273 -> 304 -0.11764
274 -> 304 0.10960
282 -> 303 0.16188
282 -> 304 0.40404
283 -> 304 0.32097
284 -> 304 -0.10690

Porphyrin **2b** (Fc A_2B_2):

Excited State 1: Singlet-AU 1.9919 eV 622.43 nm f=0.1236 <S**2>=0.000
334 -> 336 0.27517
334 -> 337 -0.25398
335 -> 336 0.44387
335 -> 337 0.35435
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -6206.80094338
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-AU 2.1325 eV 581.39 nm f=0.0790 <S**2>=0.000
328 -> 349 -0.16847
328 -> 351 0.15408
329 -> 350 -0.10327
329 -> 352 0.15541
330 -> 349 0.17736
330 -> 351 0.11455
331 -> 350 0.20316
331 -> 352 0.12706
334 -> 336 0.27617
335 -> 336 -0.22923
335 -> 337 0.36709

Excited State 3: Singlet-AG 2.1605 eV 573.86 nm f=0.0000 <S**2>=0.000
328 -> 352 -0.27197
329 -> 349 -0.25324
329 -> 351 -0.17232
330 -> 340 0.11567
330 -> 350 0.32105
330 -> 352 0.12267
331 -> 336 -0.16365
331 -> 349 0.26288
331 -> 351 -0.23467

Excited State 4: Singlet-AU 2.1678 eV 571.92 nm f=0.0002 <S**2>=0.000
328 -> 349 -0.24967
328 -> 351 -0.17325
329 -> 340 0.13171
329 -> 350 0.27862
329 -> 352 0.19336
330 -> 336 0.15772
330 -> 349 -0.24454
330 -> 351 0.25142
331 -> 350 0.15883
331 -> 352 -0.25377

Excited State 5: Singlet-AG 2.1702 eV 571.30 nm f=0.0000 <S**2>=0.000
328 -> 340 0.10726
328 -> 350 0.31183
328 -> 352 0.10662
329 -> 336 0.15341
329 -> 349 -0.24482
329 -> 351 0.24041
330 -> 352 0.29287
331 -> 349 -0.25256
331 -> 351 -0.20089

Excited State 6: Singlet-AU 2.2235 eV 557.62 nm f=0.0617 <S**2>=0.000
328 -> 336 0.11212
328 -> 349 -0.16017
328 -> 351 0.15126
329 -> 350 -0.12053
329 -> 352 0.17714
330 -> 349 0.18210
330 -> 351 0.14929
331 -> 350 0.20951
331 -> 352 0.10639

334 -> 336 -0.17348
334 -> 337 -0.23824
335 -> 336 0.33934
335 -> 337 -0.23059

Excited State 7: Singlet-AG 2.5545 eV 485.36 nm f=0.0000 <S**2>=0.000
317 -> 350 -0.10783
318 -> 349 0.10330
319 -> 336 -0.10241
319 -> 349 0.27147
320 -> 350 -0.19847
320 -> 352 -0.17351
328 -> 350 -0.23040
328 -> 352 0.10990
329 -> 351 0.28347
330 -> 352 0.20787
331 -> 349 0.17872

Excited State 8: Singlet-AU 2.5552 eV 485.22 nm f=0.0088 <S**2>=0.000
317 -> 349 0.13086
319 -> 340 -0.10109
319 -> 350 -0.20093
319 -> 352 -0.17758
320 -> 336 -0.10390
320 -> 349 0.25600
320 -> 351 -0.10819
328 -> 349 0.17280
328 -> 351 0.19337
329 -> 350 -0.16516
329 -> 352 0.23031
330 -> 351 0.20287
331 -> 350 -0.17602

Excited State 9: Singlet-AG 2.5929 eV 478.18 nm f=0.0000 <S**2>=0.000
319 -> 351 -0.22949
320 -> 350 0.17274
320 -> 352 -0.18874
322 -> 351 -0.10570
323 -> 351 0.13264
328 -> 352 0.23093
329 -> 336 0.11017
329 -> 349 -0.22006
330 -> 350 0.25758
331 -> 351 0.28392

Excited State 10: Singlet-AU 2.5941 eV 477.94 nm f=0.0044 <S**2>=0.000
317 -> 351 -0.12155
319 -> 350 0.18107
319 -> 352 -0.16889
320 -> 349 -0.10056
320 -> 351 -0.23623
321 -> 351 0.10356
323 -> 352 0.10760
328 -> 336 0.11044
328 -> 351 0.21907
329 -> 350 0.20255
330 -> 349 -0.20600
330 -> 351 -0.18053
331 -> 350 -0.15406
331 -> 352 0.23895

Excited State 11: Singlet-AU 2.9482 eV 420.54 nm f=2.1209 <S**2>=0.000
334 -> 336 0.56257
335 -> 337 -0.42629

Excited State 12: Singlet-AU 2.9906 eV 414.58 nm f=2.1421 <S**2>=0.000
334 -> 337 0.59932
335 -> 336 0.36087

Excited State 13: Singlet-AG 3.3747 eV 367.39 nm f=0.0000 <S**2>=0.000
319 -> 336 -0.12614
319 -> 349 0.24279
320 -> 350 -0.20146
320 -> 352 -0.14234
322 -> 349 0.10428
323 -> 349 -0.12432
328 -> 350 0.21325
329 -> 336 -0.10278
329 -> 351 -0.24208
330 -> 340 -0.10342
330 -> 352 -0.18427
331 -> 336 0.25448
331 -> 349 -0.16191

Excited State 14: Singlet-AU 3.3791 eV 366.92 nm f=0.0058 <S**2>=0.000
317 -> 349 -0.11600
319 -> 350 0.17495
319 -> 352 0.15787

320 -> 336 0.13072
320 -> 349 -0.24459
321 -> 349 0.10229
323 -> 350 -0.10470
328 -> 349 0.18155
328 -> 351 0.15125
329 -> 350 -0.15292
329 -> 352 0.19600
330 -> 336 0.23777
330 -> 351 0.18866
331 -> 350 -0.16007

Excited State 15: Singlet-AG 3.4651 eV 357.81 nm f=0.0000 <S**2>=0.000
317 -> 352 -0.11232
318 -> 351 -0.10731
319 -> 351 -0.29309
320 -> 350 0.19744
320 -> 352 -0.22851
322 -> 351 -0.10744
328 -> 352 -0.14077
329 -> 336 -0.26490
329 -> 349 0.14569
330 -> 350 -0.18624
331 -> 336 -0.14251
331 -> 351 -0.20149

Excited State 16: Singlet-AU 3.4776 eV 356.52 nm f=0.0101 <S**2>=0.000
317 -> 351 -0.13784
319 -> 350 0.21484
319 -> 352 -0.22711
320 -> 349 -0.11598
320 -> 351 -0.28777
321 -> 351 0.10787
328 -> 336 -0.23718
328 -> 351 -0.14793
329 -> 350 -0.14638
330 -> 336 -0.12741
330 -> 349 0.15117
330 -> 351 0.13651
331 -> 350 0.12606
331 -> 352 -0.17795

Excited State 17: Singlet-AG 3.7377 eV 331.71 nm f=0.0000 <S**2>=0.000
322 -> 336 -0.17309

322 -> 337 -0.22572
323 -> 336 -0.29140
323 -> 337 -0.20462
331 -> 336 0.36632
331 -> 349 0.10856
331 -> 351 -0.10437
332 -> 338 0.10767
333 -> 339 0.10768
335 -> 340 -0.15608

Excited State 18: Singlet-AU 3.7502 eV 330.60 nm f=1.6243 <S**2>=0.000
332 -> 339 0.48927
333 -> 338 0.48957

Excited State 19: Singlet-AG 3.7507 eV 330.56 nm f=0.0000 <S**2>=0.000
332 -> 338 0.47751
333 -> 339 0.47748

Excited State 20: Singlet-AG 3.8117 eV 325.27 nm f=0.0000 <S**2>=0.000
321 -> 340 -0.11965
322 -> 336 0.27350
322 -> 337 0.24195
323 -> 337 0.24959
330 -> 352 0.11584
331 -> 336 0.40881
331 -> 337 -0.16778
331 -> 349 0.13181

Excited State 21: Singlet-AU 3.8578 eV 321.39 nm f=0.0671 <S**2>=0.000
321 -> 336 0.20376
321 -> 337 0.13236
328 -> 336 -0.15735
329 -> 352 -0.13300
330 -> 336 0.53280
330 -> 349 0.15206
330 -> 351 -0.11814
331 -> 350 0.12743
331 -> 352 0.10282

Excited State 22: Singlet-AG 3.8950 eV 318.32 nm f=0.0000 <S**2>=0.000
328 -> 352 -0.14170
329 -> 336 0.57561
329 -> 349 0.18524
329 -> 351 -0.11455

330 -> 350 -0.13901
330 -> 352 -0.11114

Excited State 23: Singlet-AU 3.9187 eV 316.39 nm f=0.0199 <S**2>=0.000
328 -> 336 0.54240
328 -> 349 0.14414
328 -> 351 -0.12374
329 -> 350 -0.13607
329 -> 352 -0.12948
330 -> 336 0.20178
330 -> 349 0.10740
331 -> 352 -0.12266

Excited State 24: Singlet-AU 3.9460 eV 314.20 nm f=0.2510 <S**2>=0.000
316 -> 336 0.10558
316 -> 337 0.11146
320 -> 336 0.13483
320 -> 337 0.12155
321 -> 336 0.33495
321 -> 337 0.38060
322 -> 340 -0.13248
324 -> 337 0.11402
326 -> 337 0.13453
328 -> 336 0.20094
330 -> 336 -0.16551

Excited State 25: Singlet-AG 3.9739 eV 312.00 nm f=0.0000 <S**2>=0.000
324 -> 338 -0.25420
325 -> 339 -0.31218
326 -> 338 0.22680
327 -> 339 0.13685
332 -> 342 0.35563
333 -> 341 0.35807

Excited State 26: Singlet-AU 3.9739 eV 311.99 nm f=0.0002 <S**2>=0.000
324 -> 339 -0.25421
325 -> 338 -0.31219
326 -> 339 0.22666
327 -> 338 0.13687
332 -> 341 0.35805
333 -> 342 0.35578

Excited State 27: Singlet-AG 4.0399 eV 306.90 nm f=0.0000 <S**2>=0.000
322 -> 336 0.10742

322 -> 337 0.12286
323 -> 336 0.12610
327 -> 337 -0.20067
331 -> 337 0.58963
335 -> 340 0.12995

Excited State 28: Singlet-AG 4.1068 eV 301.90 nm f=0.0000 <S**2>=0.000
322 -> 336 0.14129
325 -> 337 0.18183
327 -> 336 -0.16483
327 -> 337 0.52286
331 -> 337 0.22978
335 -> 340 -0.19260

Excited State 29: Singlet-AU 4.1088 eV 301.75 nm f=0.0873 <S**2>=0.000
324 -> 337 -0.15388
326 -> 337 -0.18796
328 -> 337 -0.43397
330 -> 337 0.47893

Excited State 30: Singlet-AG 4.1600 eV 298.04 nm f=0.0000 <S**2>=0.000
323 -> 336 0.12207
329 -> 337 0.67285

Excited State 31: Singlet-AU 4.1673 eV 297.52 nm f=0.0212 <S**2>=0.000
321 -> 336 -0.11775
326 -> 337 0.12162
328 -> 337 0.43383
330 -> 337 0.49972

Excited State 32: Singlet-AU 4.2348 eV 292.77 nm f=0.0003 <S**2>=0.000
332 -> 336 0.68756

Excited State 33: Singlet-AG 4.2354 eV 292.74 nm f=0.0000 <S**2>=0.000
333 -> 336 0.70398

Excited State 34: Singlet-AU 4.2523 eV 291.57 nm f=0.0055 <S**2>=0.000
321 -> 336 -0.30465
321 -> 337 0.17723
324 -> 336 -0.13592
324 -> 337 0.25205
326 -> 336 -0.17105
326 -> 337 0.33165
328 -> 337 -0.29608

332 -> 336 0.15775

Excited State 35: Singlet-AG 4.2625 eV 290.87 nm f=0.0000 <S**2>=0.000
319 -> 336 0.11636
322 -> 336 -0.17608
323 -> 336 0.28986
325 -> 336 0.12058
327 -> 336 0.34987
327 -> 337 0.22690
331 -> 336 0.14072
335 -> 340 0.29238

Excited State 36: Singlet-AG 4.2678 eV 290.51 nm f=0.0000 <S**2>=0.000
322 -> 336 -0.21588
322 -> 337 0.33701
323 -> 336 -0.30148
323 -> 337 0.24539
327 -> 336 0.25290
327 -> 337 0.13317
329 -> 337 0.14103
331 -> 337 0.10981
334 -> 340 -0.15268

Excited State 37: Singlet-AG 4.3254 eV 286.64 nm f=0.0000 <S**2>=0.000
322 -> 336 0.32632
323 -> 337 -0.11007
325 -> 336 0.14157
327 -> 336 0.42365
335 -> 340 -0.34769

Excited State 38: Singlet-AG 4.3266 eV 286.56 nm f=0.0000 <S**2>=0.000
333 -> 337 0.69717

Excited State 39: Singlet-AU 4.3266 eV 286.56 nm f=0.0001 <S**2>=0.000
332 -> 337 0.70203

Excited State 40: Singlet-AU 4.3683 eV 283.83 nm f=0.0078 <S**2>=0.000
316 -> 337 0.11629
320 -> 337 0.13565
321 -> 336 -0.33236
321 -> 337 0.40295
324 -> 337 -0.18457
326 -> 337 -0.26663
328 -> 337 0.13824

Excited State 41: Singlet-AU 4.4082 eV 281.26 nm f=0.0504 <S**2>=0.000
321 -> 336 -0.17054
324 -> 336 0.36429
324 -> 337 0.12767
326 -> 336 0.49453
326 -> 337 0.17367

Excited State 42: Singlet-AG 4.5041 eV 275.27 nm f=0.0000 <S**2>=0.000
303 -> 336 0.10850
303 -> 337 0.14203
309 -> 336 0.13245
322 -> 336 0.29537
322 -> 337 -0.11267
323 -> 336 -0.33785
327 -> 337 0.11813
335 -> 340 0.38668

Excited State 43: Singlet-AG 4.5684 eV 271.39 nm f=0.0000 <S**2>=0.000
302 -> 340 -0.15546
303 -> 336 0.45636
303 -> 337 0.39109
322 -> 337 0.12857
334 -> 340 0.17163
335 -> 340 -0.11790

Excited State 44: Singlet-AU 4.5841 eV 270.46 nm f=0.0245 <S**2>=0.000
302 -> 336 0.48679
302 -> 337 0.45987
303 -> 340 -0.17155

Excited State 45: Singlet-AG 4.5970 eV 269.71 nm f=0.0000 <S**2>=0.000
303 -> 336 -0.13174
303 -> 337 -0.15541
322 -> 337 0.26106
323 -> 336 -0.11551
323 -> 337 -0.23591
331 -> 337 -0.12444
334 -> 340 0.46857
335 -> 338 0.10548

Excited State 46: Singlet-AU 4.6302 eV 267.77 nm f=0.0116 <S**2>=0.000
335 -> 339 0.69680

Excited State 47: Singlet-AG 4.6316 eV 267.69 nm f=0.0000 <S**2>=0.000
335 -> 338 0.68305

Excited State 48: Singlet-AG 4.6698 eV 265.50 nm f=0.0000 <S**2>=0.000
303 -> 336 0.10088
303 -> 337 -0.17015
307 -> 336 0.21773
307 -> 337 -0.11207
309 -> 336 0.36757
309 -> 337 -0.22657
315 -> 336 0.13865
322 -> 336 -0.12601
323 -> 337 0.19401
334 -> 340 0.24309

Excited State 49: Singlet-AU 4.7499 eV 261.02 nm f=0.1450 <S**2>=0.000
306 -> 336 -0.26401
306 -> 337 0.11223
308 -> 336 -0.10659
310 -> 336 0.13530
310 -> 337 -0.11036
316 -> 336 0.25184
317 -> 336 -0.13296
320 -> 336 0.44407

Excited State 50: Singlet-AG 4.7609 eV 260.42 nm f=0.0000 <S**2>=0.000
303 -> 336 -0.44795
303 -> 337 0.46560

Excited State 51: Singlet-AU 4.7818 eV 259.29 nm f=0.0683 <S**2>=0.000
306 -> 336 -0.25834
306 -> 337 0.20002
308 -> 336 -0.16589
308 -> 337 0.11062
309 -> 340 0.10699
310 -> 336 0.32566
310 -> 337 -0.14292
316 -> 336 -0.10127
320 -> 336 -0.29451
321 -> 336 0.18626

Excited State 52: Singlet-AU 4.7870 eV 259.00 nm f=0.0045 <S**2>=0.000
302 -> 336 -0.46300
302 -> 337 0.47715

320 -> 336 -0.11793

Excited State 53: Singlet-AG 4.7877 eV 258.96 nm f=0.0000 <S**2>=0.000
301 -> 336 -0.14343
309 -> 336 -0.22934
309 -> 337 0.12774
311 -> 336 -0.13595
311 -> 337 0.10466
315 -> 336 -0.12987
315 -> 337 0.10958
318 -> 336 -0.12352
322 -> 337 -0.26540
323 -> 337 0.34519
334 -> 340 0.27413

Excited State 54: Singlet-AG 4.8253 eV 256.95 nm f=0.0000 <S**2>=0.000
318 -> 336 -0.11537
319 -> 336 0.61114
320 -> 340 0.10786
323 -> 336 -0.11266

Excited State 55: Singlet-AU 4.8390 eV 256.22 nm f=0.2395 <S**2>=0.000
313 -> 338 -0.13255
314 -> 339 -0.11389
324 -> 339 -0.10099
325 -> 338 -0.12829
326 -> 339 0.10315
332 -> 341 -0.14221
332 -> 346 -0.42221
333 -> 342 -0.14199
333 -> 345 0.42399

Excited State 56: Singlet-AG 4.8390 eV 256.22 nm f=0.0000 <S**2>=0.000
313 -> 339 -0.13258
314 -> 338 -0.11397
324 -> 338 -0.10091
325 -> 339 -0.12804
326 -> 338 0.10296
332 -> 342 -0.14172
332 -> 345 0.42408
333 -> 341 -0.14202
333 -> 346 -0.42252

Excited State 57: Singlet-AU 4.8657 eV 254.81 nm f=0.5624 <S**2>=0.000

308 -> 336 -0.10958
310 -> 336 -0.10317
316 -> 336 0.37224
320 -> 336 -0.20211
324 -> 339 0.17171
325 -> 338 0.21291
326 -> 339 -0.15970
332 -> 341 0.22212
332 -> 346 -0.13475
333 -> 342 0.22055
333 -> 345 0.13525

Excited State 58: Singlet-AG 4.8662 eV 254.79 nm f=0.0000 <S**2>=0.000
324 -> 338 0.24401
325 -> 339 0.30105
326 -> 338 -0.22258
327 -> 339 -0.13612
332 -> 342 0.31035
332 -> 345 0.18521
333 -> 341 0.31278
333 -> 346 -0.18459

Excited State 59: Singlet-AU 4.8665 eV 254.77 nm f=0.9066 <S**2>=0.000
308 -> 336 -0.10621
310 -> 336 -0.11627
316 -> 336 0.38081
320 -> 336 -0.20254
324 -> 339 -0.17289
325 -> 338 -0.21266
326 -> 339 0.15492
332 -> 341 -0.21979
332 -> 346 0.12676
333 -> 342 -0.21816
333 -> 345 -0.12724

Excited State 60: Singlet-AG 4.9257 eV 251.71 nm f=0.0000 <S**2>=0.000
307 -> 336 -0.14984
317 -> 340 0.14206
318 -> 336 0.59629
319 -> 336 0.10888
323 -> 337 0.11950
334 -> 340 0.10877

Excited State 61: Singlet-AU 4.9351 eV 251.23 nm f=0.0020 <S**2>=0.000

308 -> 336 -0.14143
310 -> 336 0.12155
317 -> 336 0.59645
318 -> 340 0.14109
320 -> 336 0.12988

Excited State 62: Singlet-AG 5.0484 eV 245.59 nm f=0.0000 <S**2>=0.000
309 -> 336 0.20869
309 -> 337 0.17863
313 -> 337 -0.13815
315 -> 337 0.44875
326 -> 343 0.12332
327 -> 344 0.17199
334 -> 338 -0.10840
335 -> 343 0.19005

Excited State 63: Singlet-AU 5.0537 eV 245.33 nm f=0.0868 <S**2>=0.000
306 -> 336 0.13818
306 -> 337 0.17594
310 -> 336 -0.17725
312 -> 337 0.29972
314 -> 337 -0.19974
316 -> 337 -0.17680
320 -> 337 -0.24248
321 -> 337 0.17352
326 -> 344 -0.10741
327 -> 343 -0.15094
334 -> 339 0.14601
335 -> 344 -0.17207

Excited State 64: Singlet-AG 5.0717 eV 244.46 nm f=0.0000 <S**2>=0.000
312 -> 338 0.24085
313 -> 339 0.41338
314 -> 338 0.36323
315 -> 339 0.13916
332 -> 345 0.13170
333 -> 346 -0.13116
334 -> 338 0.21539

Excited State 65: Singlet-AU 5.0717 eV 244.46 nm f=0.0020 <S**2>=0.000
312 -> 339 0.24026
313 -> 338 0.41291
314 -> 339 0.36280
315 -> 338 0.13888

332 -> 346 -0.13079
333 -> 345 0.13160
334 -> 339 0.21562

Excited State 66: Singlet-AU 5.0757 eV 244.27 nm f=0.0074 <S**2>=0.000
313 -> 338 -0.14047
314 -> 339 -0.11499
320 -> 337 0.10432
334 -> 339 0.64402

Excited State 67: Singlet-AG 5.0759 eV 244.26 nm f=0.0000 <S**2>=0.000
313 -> 339 -0.13909
314 -> 338 -0.11430
334 -> 338 0.65907

Excited State 68: Singlet-AU 5.0977 eV 243.21 nm f=0.0630 <S**2>=0.000
306 -> 337 -0.15332
312 -> 337 0.20985
314 -> 337 -0.15905
316 -> 337 0.19475
320 -> 337 0.37684
321 -> 337 -0.16295
324 -> 344 -0.10134
326 -> 344 -0.12753
327 -> 343 -0.17913
334 -> 339 -0.11186
335 -> 344 -0.21725

Excited State 69: Singlet-AG 5.1293 eV 241.72 nm f=0.0000 <S**2>=0.000
307 -> 337 0.16276
309 -> 336 0.15375
309 -> 337 0.37167
311 -> 337 0.17818
315 -> 336 0.18868
324 -> 343 -0.10951
326 -> 343 -0.13888
327 -> 344 -0.19852
334 -> 340 -0.10711
335 -> 343 -0.27469

Excited State 70: Singlet-AU 5.1571 eV 240.41 nm f=0.0425 <S**2>=0.000
306 -> 336 0.10889
306 -> 337 0.27610
308 -> 337 0.17989

310 -> 336 -0.16379
310 -> 337 -0.28544
312 -> 336 0.10062
320 -> 337 0.39586
321 -> 337 -0.10576
335 -> 344 0.13456

Excited State 71: Singlet-AG 5.1712 eV 239.76 nm f=0.0000 <S**2>=0.000
301 -> 336 -0.10967
309 -> 337 -0.11594
319 -> 337 0.61105
322 -> 337 0.15061
323 -> 337 -0.16207

Excited State 72: Singlet-AG 5.2366 eV 236.77 nm f=0.0000 <S**2>=0.000
301 -> 336 0.25809
301 -> 337 0.16504
307 -> 336 -0.24052
309 -> 336 -0.15723
311 -> 336 0.31193
315 -> 336 0.27955
318 -> 337 0.12705
319 -> 337 0.15254

Excited State 73: Singlet-AU 5.2618 eV 235.63 nm f=0.0597 <S**2>=0.000
312 -> 336 -0.12576
312 -> 337 0.30854
314 -> 337 -0.22657
316 -> 337 0.22953
320 -> 337 -0.11948
324 -> 336 -0.18455
326 -> 336 0.16506
326 -> 344 0.10244
327 -> 343 0.15804
335 -> 344 0.30612

Excited State 74: Singlet-AG 5.2644 eV 235.52 nm f=0.0000 <S**2>=0.000
309 -> 337 -0.15193
311 -> 337 -0.13282
315 -> 336 -0.17349
315 -> 337 0.29092
325 -> 336 0.37108
327 -> 336 -0.15584
327 -> 344 -0.12568

335 -> 343 -0.28341

Excited State 75: Singlet-AU 5.2762 eV 234.99 nm f=0.0372 <S**2>=0.000
310 -> 337 -0.14376
316 -> 337 0.34631
320 -> 337 -0.17246
324 -> 336 0.43243
326 -> 336 -0.31954

Excited State 76: Singlet-AG 5.2814 eV 234.76 nm f=0.0000 <S**2>=0.000
307 -> 337 0.10231
309 -> 337 0.14841
315 -> 337 -0.23253
325 -> 336 0.53504
327 -> 336 -0.16418
335 -> 343 0.18574

Excited State 77: Singlet-AU 5.2854 eV 234.58 nm f=0.0349 <S**2>=0.000
306 -> 337 0.11211
310 -> 337 -0.24579
312 -> 337 -0.17371
314 -> 337 0.11454
316 -> 337 0.35765
320 -> 337 -0.17136
324 -> 336 -0.30191
326 -> 336 0.20139
335 -> 344 -0.17425

Excited State 78: Singlet-AG 5.3243 eV 232.86 nm f=0.0000 <S**2>=0.000
301 -> 336 -0.17491
301 -> 337 0.15399
307 -> 337 -0.16172
311 -> 336 -0.11770
311 -> 337 0.15237
318 -> 337 0.51526
319 -> 337 -0.16087

Excited State 79: Singlet-AU 5.3411 eV 232.13 nm f=0.0056 <S**2>=0.000
306 -> 336 0.25576
307 -> 340 -0.13075
307 -> 350 -0.10107
308 -> 336 -0.32283
308 -> 349 0.13876
317 -> 336 -0.14043

317 -> 337 0.40596
335 -> 351 0.10985

Excited State 80: Singlet-AG 5.3577 eV 231.41 nm f=0.0000 <S**2>=0.000
307 -> 336 0.25652
307 -> 349 -0.13081
308 -> 340 0.10473
308 -> 350 0.10076
309 -> 336 -0.24115
311 -> 336 -0.22913
313 -> 336 -0.10324
315 -> 336 0.33828
315 -> 337 0.10292
318 -> 336 0.11982
335 -> 352 -0.10122

Excited State 81: Singlet-AU 5.3630 eV 231.19 nm f=0.0075 <S**2>=0.000
310 -> 336 0.11393
312 -> 336 0.42631
314 -> 336 -0.30184
317 -> 337 -0.13172
324 -> 337 0.28488
326 -> 337 -0.20760

Excited State 82: Singlet-AG 5.3692 eV 230.92 nm f=0.0000 <S**2>=0.000
307 -> 336 0.17017
315 -> 336 -0.11253
325 -> 337 0.58649
327 -> 337 -0.21067

Excited State 83: Singlet-AU 5.3746 eV 230.68 nm f=0.0166 <S**2>=0.000
308 -> 336 0.15155
312 -> 336 -0.14819
312 -> 337 -0.10688
314 -> 336 0.10532
317 -> 337 0.30409
324 -> 337 0.41780
326 -> 337 -0.33489

Excited State 84: Singlet-AU 5.3794 eV 230.48 nm f=0.0043 <S**2>=0.000
306 -> 336 -0.17654
308 -> 336 0.18480
308 -> 337 -0.12305
308 -> 349 -0.10450

312 -> 336 0.20707
314 -> 336 -0.14638
317 -> 337 0.41214
324 -> 337 -0.21552
326 -> 337 0.16056

Excited State 85: Singlet-AG 5.3851 eV 230.24 nm f=0.0000 <S**2>=0.000
301 -> 336 -0.12914
307 -> 336 -0.27097
307 -> 349 0.11030
309 -> 337 -0.10858
311 -> 336 -0.25910
315 -> 336 0.27173
315 -> 337 0.13715
318 -> 337 -0.18253
325 -> 337 0.25560
335 -> 347 -0.11076

Excited State 86: Singlet-AG 5.4360 eV 228.08 nm f=0.0000 <S**2>=0.000
300 -> 336 -0.10015
301 -> 336 0.19173
301 -> 337 -0.27478
311 -> 336 -0.19769
311 -> 337 -0.13494
315 -> 336 0.10858
318 -> 337 0.26621
335 -> 347 0.29615

Excited State 87: Singlet-AU 5.4371 eV 228.03 nm f=0.0136 <S**2>=0.000
306 -> 336 0.27452
308 -> 336 0.29952
310 -> 336 0.37465
311 -> 340 0.12928
316 -> 336 0.21706
335 -> 351 0.11989

Excited State 88: Singlet-AG 5.4533 eV 227.36 nm f=0.0000 <S**2>=0.000
301 -> 337 0.18519
307 -> 336 -0.16278
309 -> 336 0.13884
310 -> 352 -0.11243
311 -> 337 0.12812
311 -> 351 -0.10328
316 -> 350 -0.11910

318 -> 337 -0.18529
319 -> 351 -0.10915
322 -> 351 0.10152
323 -> 351 -0.16517
335 -> 350 0.29512
335 -> 352 -0.24291

Excited State 89: Singlet-AU 5.4625 eV 226.98 nm f=0.0262 <S**2>=0.000
306 -> 336 -0.17066
310 -> 336 -0.11023
310 -> 349 0.10068
310 -> 351 0.12290
316 -> 351 -0.13859
319 -> 350 -0.13022
322 -> 350 0.11285
323 -> 350 -0.17589
323 -> 352 0.13207
335 -> 349 0.28626
335 -> 351 0.35931

Excited State 90: Singlet-AU 5.4640 eV 226.91 nm f=1.4930 <S**2>=0.000
324 -> 341 -0.18416
325 -> 342 -0.23374
326 -> 341 0.19521
327 -> 342 0.13044
327 -> 347 -0.11989
335 -> 341 0.14676
335 -> 348 0.45920

Excited State 91: Singlet-AG 5.4701 eV 226.66 nm f=0.0000 <S**2>=0.000
301 -> 336 -0.25934
301 -> 337 -0.21100
310 -> 350 0.10508
311 -> 336 0.23151
311 -> 337 -0.14468
327 -> 339 0.12533
335 -> 343 0.10325
335 -> 350 0.27985

Excited State 92: Singlet-AG 5.4746 eV 226.47 nm f=0.0000 <S**2>=0.000
301 -> 336 0.30202
309 -> 336 0.10695
311 -> 336 -0.10486
324 -> 342 -0.19237

325 -> 341 -0.24159
326 -> 342 0.19259
327 -> 341 0.13214
335 -> 342 0.11056
335 -> 347 -0.27836

Excited State 93: Singlet-AU 5.4836 eV 226.10 nm f=0.1557 <S**2>=0.000
305 -> 338 0.10262
324 -> 339 0.23160
324 -> 341 -0.13679
325 -> 338 0.15473
325 -> 342 -0.17105
326 -> 339 0.24031
326 -> 341 0.13523
327 -> 338 0.33451
328 -> 339 0.10176
335 -> 344 0.11958
335 -> 348 -0.24603

Excited State 94: Singlet-AG 5.4857 eV 226.01 nm f=0.0000 <S**2>=0.000
301 -> 337 0.12925
324 -> 338 0.20590
325 -> 339 0.13750
325 -> 341 -0.12667
326 -> 338 0.21316
327 -> 339 0.29634
335 -> 347 0.32710

Excited State 95: Singlet-AG 5.5180 eV 224.69 nm f=0.0000 <S**2>=0.000
301 -> 336 0.11638
324 -> 338 0.15077
324 -> 342 0.25809
325 -> 341 0.31651
326 -> 338 0.15760
326 -> 342 -0.22039
327 -> 339 0.21695
327 -> 341 -0.12889
335 -> 343 0.17597
335 -> 347 -0.22053

Excited State 96: Singlet-AU 5.5193 eV 224.64 nm f=1.4880 <S**2>=0.000
324 -> 339 0.14975
324 -> 341 0.26087
325 -> 342 0.31505

326 -> 339 0.15657
326 -> 341 -0.22138
327 -> 338 0.21536
327 -> 342 -0.12774
335 -> 344 0.18848
335 -> 348 0.24981

Excited State 97: Singlet-AU 5.5653 eV 222.78 nm f=0.0919 <S**2>=0.000
316 -> 349 -0.12708
317 -> 351 -0.11502
323 -> 352 -0.17152
335 -> 349 0.42222
335 -> 351 -0.27002

Excited State 98: Singlet-AG 5.6010 eV 221.36 nm f=0.0000 <S**2>=0.000
301 -> 337 0.11059
311 -> 337 0.10024
317 -> 352 0.11808
318 -> 351 0.10225
319 -> 349 -0.10887
323 -> 349 -0.15624
323 -> 351 0.13488
335 -> 350 0.28461
335 -> 352 0.41665

Excited State 99: Singlet-AG 5.6190 eV 220.65 nm f=0.0000 <S**2>=0.000
315 -> 348 -0.11054
324 -> 343 -0.15069
326 -> 343 -0.20319
327 -> 339 -0.10312
327 -> 344 -0.21986
335 -> 342 -0.29129
335 -> 343 0.34986
335 -> 347 0.10214

Excited State 100: Singlet-AU 5.6262 eV 220.37 nm f=0.0316 <S**2>=0.000
315 -> 347 0.10133
324 -> 344 -0.13878
326 -> 344 -0.19397
327 -> 343 -0.20753
335 -> 341 -0.30930
335 -> 344 0.35316
335 -> 349 0.13011

Excited State 101: Singlet-AU 5.6511 eV 219.40 nm f=0.0018 <S**2>=0.000
304 -> 339 -0.19178
305 -> 338 -0.18804
312 -> 341 -0.12619
313 -> 342 -0.20971
314 -> 341 -0.18085
324 -> 346 0.18605
325 -> 345 -0.22851
326 -> 346 -0.16183
332 -> 354 0.18904
333 -> 353 0.18919
335 -> 341 0.29106

Excited State 102: Singlet-AG 5.6512 eV 219.40 nm f=0.0000 <S**2>=0.000
304 -> 338 -0.19304
305 -> 339 -0.18941
312 -> 342 -0.12615
313 -> 341 -0.21280
314 -> 342 -0.18117
324 -> 345 -0.18874
325 -> 346 0.22919
326 -> 345 0.16300
332 -> 353 0.19085
333 -> 354 0.19068
335 -> 342 0.27735

Excited State 103: Singlet-AU 5.6612 eV 219.01 nm f=0.0000 <S**2>=0.000
332 -> 339 0.49999
333 -> 338 -0.49982

Excited State 104: Singlet-AG 5.6612 eV 219.01 nm f=0.0000 <S**2>=0.000
332 -> 338 -0.49973
333 -> 339 0.49992

Excited State 105: Singlet-AG 5.6786 eV 218.34 nm f=0.0000 <S**2>=0.000
335 -> 342 0.54496
335 -> 343 0.19450
335 -> 347 0.18888

Excited State 106: Singlet-AU 5.6797 eV 218.29 nm f=0.0277 <S**2>=0.000
327 -> 343 -0.10500
335 -> 341 0.53154
335 -> 344 0.21995
335 -> 348 -0.18651

Excited State 107: Singlet-AG 5.7745 eV 214.71 nm f=0.0000 <S**2>=0.000
300 -> 336 -0.24471
300 -> 337 0.16799
301 -> 336 0.10603
301 -> 337 -0.19749
309 -> 337 -0.13770
311 -> 337 0.43883
311 -> 351 0.10893
315 -> 337 0.10784

Excited State 108: Singlet-AU 5.7992 eV 213.80 nm f=0.0023 <S**2>=0.000
308 -> 336 -0.10437
310 -> 337 -0.12722
311 -> 350 0.11082
316 -> 351 -0.11762
328 -> 361 -0.11617
328 -> 364 0.15441
328 -> 369 -0.16748
328 -> 371 0.11957
329 -> 340 0.11752
329 -> 359 0.10052
329 -> 360 -0.13456
329 -> 370 -0.10629
331 -> 340 0.18553
331 -> 365 0.18658
331 -> 368 -0.11795
331 -> 370 -0.12004

Excited State 109: Singlet-AG 5.8129 eV 213.29 nm f=0.0000 <S**2>=0.000
300 -> 337 0.11973
301 -> 337 -0.11530
307 -> 336 -0.10056
311 -> 337 0.18404
328 -> 340 0.15446
328 -> 360 -0.10724
328 -> 365 0.15562
328 -> 370 -0.15050
329 -> 358 0.10412
329 -> 361 -0.17789
330 -> 359 0.10059
330 -> 360 -0.12204
331 -> 364 0.15171
331 -> 369 -0.16598

331 -> 371 0.10433

Excited State 110: Singlet-AG 5.8218 eV 212.97 nm f=0.0000 <S**2>=0.000
300 -> 336 -0.11707
334 -> 343 0.65344

Excited State 111: Singlet-AU 5.8466 eV 212.06 nm f=0.0115 <S**2>=0.000
310 -> 337 0.10221
334 -> 344 0.62916

Excited State 112: Singlet-AU 5.8502 eV 211.93 nm f=0.0408 <S**2>=0.000
304 -> 339 -0.12132
305 -> 338 -0.11909
306 -> 337 0.23225
308 -> 337 0.16961
310 -> 337 0.33398
316 -> 337 0.15065
332 -> 354 -0.13132
333 -> 353 -0.13116
334 -> 344 -0.20620

Excited State 113: Singlet-AG 5.8529 eV 211.83 nm f=0.0000 <S**2>=0.000
304 -> 338 0.30338
305 -> 339 0.29844
332 -> 353 0.32779
333 -> 354 0.32781

Excited State 114: Singlet-AU 5.8544 eV 211.78 nm f=0.0122 <S**2>=0.000
304 -> 339 0.27931
305 -> 338 0.27501
310 -> 337 0.15219
332 -> 354 0.30276
333 -> 353 0.30306

Excited State 115: Singlet-AU 5.8700 eV 211.22 nm f=0.0262 <S**2>=0.000
306 -> 337 -0.11100
310 -> 337 -0.12318
329 -> 359 -0.10646
329 -> 360 0.12625
330 -> 358 -0.13409
330 -> 361 0.21635
330 -> 375 0.14010
331 -> 338 0.10132
331 -> 340 0.31187

331 -> 359 0.11393
331 -> 360 -0.16157

Excited State 116: Singlet-AG 5.8815 eV 210.80 nm f=0.0000 <S**2>=0.000
307 -> 337 0.15821
310 -> 350 -0.10926
311 -> 351 0.16543
316 -> 350 -0.16369
318 -> 349 0.11653
328 -> 340 0.16804
328 -> 359 0.10987
328 -> 360 -0.15893
329 -> 361 -0.12007
329 -> 364 0.11798
329 -> 369 -0.10017
330 -> 340 0.10653
330 -> 365 0.10973
331 -> 361 -0.13908

Excited State 117: Singlet-AG 5.8873 eV 210.59 nm f=0.0000 <S**2>=0.000
300 -> 336 0.23675
328 -> 365 -0.14640
328 -> 368 0.10090
329 -> 358 0.10443
329 -> 361 -0.16487
329 -> 375 -0.11567
330 -> 340 0.19374
330 -> 359 0.13930
330 -> 360 -0.19140
331 -> 361 0.13192
331 -> 364 -0.13743
331 -> 369 0.13860
334 -> 343 0.10994

Excited State 118: Singlet-AU 5.8900 eV 210.50 nm f=0.0139 <S**2>=0.000
306 -> 337 -0.14829
310 -> 337 -0.18691
316 -> 349 0.10332
317 -> 349 0.11464
318 -> 350 -0.13334
328 -> 361 -0.15008
328 -> 375 -0.10406
329 -> 340 0.20991
329 -> 359 0.10431

329 -> 360 -0.15403
330 -> 364 0.14566
330 -> 369 -0.13530
330 -> 371 0.10128
331 -> 365 -0.15391
331 -> 368 0.10528
331 -> 372 -0.10815

Excited State 119: Singlet-AG 5.9033 eV 210.03 nm f=0.0000 <S**2>=0.000
300 -> 336 0.23039
307 -> 337 0.36357
308 -> 350 -0.10149
309 -> 337 -0.18911
330 -> 340 -0.12168
330 -> 365 -0.12553
331 -> 364 0.11720
331 -> 369 -0.12029

Excited State 120: Singlet-AG 5.9079 eV 209.86 nm f=0.0000 <S**2>=0.000
330 -> 338 -0.12520
331 -> 339 0.67371